

JPRS-UCH-89-003
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UDC 541.183

Conductometric Study of Reaction of 18-Crown-6 With Alkali Metal Cations in Cationites

18410010c Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKIYE NAUKI No 4, Jul 88 (manuscript received 12 Jun 86) pp 50-53

[Article by G.N. Altshuler and M.A. Khalyapina, Coal Institute, Siberian Department USSR Academy of Sciences]

[Abstract] The sorption of macrocyclic polyesters (crown esters) from aqueous solutions with cationites in the form of alkali metal cations may serve as a basis for the separation of individual compounds from mixtures of solutions. In the present work KU-2-4 sulfonate and KB-4-2 carboxyl cationites in K^{plus} and Rb^{plus} forms were used with water-soluble macrocyclic 18-crown-6 polyester complexed with acetonitrile. The crown ester was separated from the complex by vacuum distillation of the acetonitrile. An aqueous solution of the polyester was brought to equilibrium with the sorbent under dynamic conditions at 298.15 K, and conductivity was determined in a standard cell. Solutions similar in conductivity to that of the ionite layer were prepared by adding electrolyte to the macrocyclic polyester solution. Calculations of complex formation constants and mobilities of counter-ions in the cationites indicate that a possibility of membrane separation of potassium and rubidium counter-cations exists. Figures 2; references 7: 6 Russian, 1 Western.

UDC 536.6

Study of Structure of Glycerine and Its Solutions in Plain and Heavy Water by Using Dielectric Spectroscopy

18410019c Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 57 No 7, Jul 88 (manuscript received 30 Mar 87) pp 1797-1803

[Article by U. B. Khudayarov and V. N. Khudayberdiyev, Heat Physics Division, UzSSR Academy of Sciences, Tashkent]

[Abstract] Glycerine can be used as a model for studying the specifics of the molecular interactions of associated liquids. Together with its aqueous solutions, glycerine also plays an important role in the biophysical processes taking place in the cell, and it is used in the production of various compounds. Therefore, information on the structure and properties of glycerine is vital not only to the physical chemistry of the liquid state but also for clarifying the mechanisms of molecular processes in biological media and for optimizing many technological processes. Although the physicochemical properties and structure of glycerine and its solutions have been studied

previously using acoustic, magnetic resonance, and optical methods, dielectric spectra and the molecular processes causing dielectric relaxation in the liquid phase have never been studied experimentally before. In the present work a systematic study was carried out on the complex dielectric permeability of glycerine and its solutions in plain and heavy water. Dielectric permeability and its losses over the frequency range of 40 Hz to 17 GHz and probable mechanisms for observed dielectric relaxation are presented. Figures 2; references 15: 9 Russian, 6 Western.

UDC 661.871

Study of Equilibrium of Thermal Dissociation of Manganese Nitrate in Presence of Nitrates of Alkali Metals and Alkali-earth Metals

18410045a Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 61 No 9, Sep 88 (manuscript received 16 Jul 87) pp 1953-1957

[Article by S. S. Markov, A. A. Krasilnikov, L. B. Belyayeva, and A. S. Markov, Institute of Applied Chemistry]

[Abstract] A study examined the effect of nitrates of alkali metals and alkali-earth metals on the equilibrium of the thermal dissociation of manganese nitrate. The possibility of calculating the equilibrium fraction of the total mass of manganese nitrate from the composition of the starting solution was discussed, and the conditions of the process' occurrence was determined. The equilibrium of the thermal dissociation of manganese nitrate in aqueous solutions of Mg, Ca, K, and Na nitrates was established. The equilibrium fraction of the total mass of the manganese nitrate correlated with the ratio of the fractions of the total mass of Ca and Mg in the starting solution. There was a linear correlation with the parameter χ in those regions of its change from 0 up to 0.6 and from 0.6 up to 0.75. The presence of K and Na nitrates in the system decreased the degree of manganese nitrate dissociation. The effect of these salts on the equilibrium fraction of the total mass of manganese nitrate in the solution increased as the temperature increased. The equilibrium fraction of the total mass of manganese nitrate can be calculated with a relative error of no more than 11 percent by using data concerning the composition of the starting solution and the working temperature. Figures 3; references 14: 13 Russian; 1 Western.

UDC541.183

Oxidation of Carbon Adsorbents with Ozone

18410131a Kiev KHIMICHESKAYA TEKHNLOGIYA in Russian No 1, Jan-Feb 89 (manuscript received 16 Feb 87) pp 12-16

[Article by V. G. Aleynikov, B. B. Donster, and T. N. Burushkina, Surface Chemistry Institute, Kiev]

[Abstract] Oxidized carbon adsorbents have high cation exchange selectivity, and both thermal and radiational stability. They may be prepared by treatment with oxidizing solutions although this results in altering the

quantity of surface protogenic groups over a wide range under the same treatment conditions. Oxidation with air oxygen or ozone-oxygen mixtures has also proved unsatisfactory owing to excessive porosity and laminar scorching of the particles. The feasibility of imparting ion exchange properties to activated charcoal with ozone-oxygen mixtures has been demonstrated previously, although this resulted in surface oxygen compounds with low heat resistance and considerable changes in carbon adsorbent mass due to extra-diffusional factors. In the present work a study was made of the effects of the composition of ozone-air mixtures and treatment temperatures of various carbon adsorbents on the formation of surface protogenic groups and the propagation of the oxidation process. Activated carbons from porous polyvinylbenzene, resin KU-1, and decalcified activated charcoal were treated with low concentrations of ozone-air mixtures. The degree of ozone conversion and modification of acid groups dropped significantly with the time and temperature of treatment. The rate of formation of cation exchange groups changes with the change in specific surface of the adsorbent and the ozone concentration in the mixture. The ion exchange capacity of the oxidized samples was 5-10 mmoles per gram. The rate of formation of protogenic groups decreases if oxides of nitrogen are present in the ozone-air mixture, although water vapor has a favorable effect on the modification process. Figures 4; references 10: 9 Russian, 1 Western.

UDC532.62.003.1

Engineering-Economic Evaluation of Membrane Extraction Processes

18410131c Kiev *KHIMICHESKAYA TEKHNLOGIYA* in Russian No 1, Jan-Feb 89 (manuscript received 11 Feb 88) pp 57-63

[Article by S. Yu. Ivakhno, V. Yu. Gusev, D. B. Kadosov, and A. V. Rogatinskiy, Chemical Technology Institute imeni D. I. Mendeleyev, Moscow]

[Abstract] Membrane extraction (pertraction) is becoming an increasingly practical means of leaching materials from industrial waste effluents. Three basic variants of the process are 1) extraction through free liquid membranes; 2) extraction through liquid membranes impregnated in a porous material; 3) membrane extraction in multiple emulsions. Pertractors with free liquid membranes are currently used in the USSR and Peoples Republic of Bulgaria, while impregnated membranes and associated equipment, and the multiple emulsion techniques are being developed in other countries. Unfortunately, in selecting a specific method of membrane extraction and its pertractor, developers limit themselves to a qualitative description of its advantages and disadvantages without giving a comparative engineering-economic analysis. In the present work a method for making such an evaluation is presented and used as an example for comparing the three methods for extraction of aromatic amines from aqueous solutions. It is demonstrated that a pertractor with a free membrane is the most economical.

The impregnated membrane technique is more costly owing to the high cost of the membrane material. Extraction through free liquid membranes requires less operating costs than membrane extraction in multiple emulsions. Figures 3; references 2 (Russian).

UDC678.742.3:620.17.7.178.156

Effect of Isotactic Polypropylene Structure on Mechanical Properties of Coatings

18410131d Kiev *KHIMICHESKAYA TEKHNLOGIYA* in Russian No 1, Jan-Feb 89 (manuscript received 20 Oct 87) pp 87-89

[Article by L. N. Yakubenko, Colloidal Chemistry and Hydrochemistry Institute, Kiev]

[Abstract] Polypropylene coatings have many applications and could be used for electrical insulation and protective-decorative purposes. Although they have high resistance to electrical load, heat, atmospheric and chemical corrosion, their major drawback is low impact strength. In the present work a study was made of those factors which have an effect on the mechanical properties of polypropylene coatings. A crystallizing isotactic polypropylene (3.8 percent atactic) having a molecular weight of 50,000 was chosen. Coatings were made by electrophoresis from hydrocarbon solvents. Hardness was determined in accordance with GOST 5233-67 on a hardness meter having a diamond pyramid. Impact strength was determined in accordance with GOST 4765-73 on a U-1A device. Crystallization conditions were varied by adding 0.2 and 2 percent A-380 aerosil for crystal seeding. The hypomolecular structure of the crystallized polymer has a great effect on its physical-mechanical properties. This in turn is determined by the crystallization conditions. Microphotographs of isotactic polypropylene etched with para-xylene show well-defined spherulites which grow from the seeding nuclei until they collide with one another. If the coating is tempered in air, the size of the spherulites is smaller and the impact strength of the coating is greater. Spherulite size can also be regulated by varying the concentration of crystallization nuclei. Figures 3; references 3 (Russian).

UDC661.143(088.8)

Method for Treating Iron Oxide Pigment for Coating Luminophors

18410131e Kiev *KHIMICHESKAYA TEKHNLOGIYA* in Russian No 1, Jan-Feb 89 (manuscript received 26 May 87) pp 89-92

[Article by N. I. Smirdova, R. A. Lyakh, T. V. Smityukh, and G. D. Maskalyuk, Physical Chemistry Institute, Odessa]

[Abstract] Luminophors, used in the production of color television CRTs, are surface coated with a pigment layer to adjust the radiation spectrum and improve image contrast. The color characteristics of the pigment and the amount

needed for pigmentation depend on the degree of dispersion. Finely ground pigments of less than one micron particle size are optimum for adsorption on the luminophor surface to form a uniform thin film. Although various types of mills are used to fine grind the material, ball mills are the most widely used. In the present work, red iron oxide

pigment was wet and dry ground in porcelain and steel ball mills, and in a UDA disintegrator at 15,000, 18,000 and 24,000 rpm and various dispersion media. A 2.5 percent solution of sodium pyrophosphate appears to be the optimum dispersion medium with UDA grinding. References 5 (Russian).

UDC 541.128.13:541.127-14:542.941.7:546
92'26:547.592.2

Liquid Phase Hydrogenation of Cyclohexene Over Platinum and Palladium Catalysts

18410035a Moscow KINETIKA I KATALIZ in Russian
Vol 29 No 4, Jul-Aug 88 (manuscript received
19 May 87) pp 815-819

[Article by D. Yu. Murzin, V. Yu. Konyukhov, N. V. Kulkova, and M. I. Temkin, Physical Chemistry SRI imeni L. Ya. Karpov, Moscow]

[Abstract] A study examined the kinetics of liquid phase hydrogenation of cyclohexene over Pt and Pd catalysts. The initial experiments, which were conducted with the same catalysts as those previously used for the hydrogenation of benzene, showed that hydrogenation of cyclohexene is faster than that of benzene. Therefore, catalysts containing 0.5 percent Pt or Pd on carbon were used instead of 5 percent as for benzene. The experiments were conducted in an oscillating steel reactor at hydrogen pressures ranging from 0.09 to 2.1 MPa and temperatures of 35 to 85°C for palladium and 16 to 49°C for platinum. The oscillation frequency was 150 per minute at 15 cm amplitude. The catalysts' particle size was below 50 μm and the surface of the metal per gram of catalyst was 0.6 square meters for Pt and 0.4 for Pd. The results indicate that the cyclohexene hydrogenation reaction rate follows the same kinetic equation as that established previously for hydrogenation of the benzene ring. References 10: 7 Russian, 3 Western.

UDC 541.128.3:542.941.7:546.262.3-31:
546.73'74-44:549.975

Effect of Nature of Carrier on Catalytic Properties of Cobalt and Nickel Catalysts in Carbon Monoxide Hydrogenation Reactions

18410035b Moscow KINETIKA I KATALIZ in Russian
Vol 29 No 4, Jul-Aug 88 (manuscript received
22 Apr 87) pp 820-824

[Article by Ye. V. Prokhorenko, N. V. Pavlenko, and G. I. Golodets, Physical Chemistry Institute imeni L. V. Pisarzhevskiy, Kiev]

[Abstract] Previous works have studied the catalytic properties of transition metals on a γ -alumina carrier for hydrogenation reactions of carbon monoxide to methane and its homologues. However, there is still no unified viewpoint that would make it possible to explain the effects of the chemical composition of the metal-containing systems on their catalytic properties. The present work examines the effects of the chemical nature of eight oxide carriers on the catalytic effects of Co and Ni. The study showed that the particle size of these metals depends on the carrier, which also affects activity and selectivity in the carbon monoxide hydrogenation reactions. Selectivity is also a function of the acid-base

properties of the carrier, as manifested in the intermediate reactions of adsorbed oxygen-containing complexes with Lewis acid sites located at the metal-carrier interface. Figures 2; references 19: 16 Russian, 3 Western.

UDC 541.128.3:541.127:547.21:542.924

Effect of Active Sites on Catalytic Pyrolysis of Hydrocarbons

18410035c Moscow KINETIKA I KATALIZ in Russian
Vol 29 No 4, Jul-Aug 88 (manuscript received
6 May 87) pp 825-830

[Article by N. A. Vasilyeva and R. A. Buyanov, Catalysis Institute, Novosibirsk]

[Abstract] In a previous work it was demonstrated that hydrocarbon pyrolysis in the presence of a catalyst takes place through a heterogeneous-homogeneous radical-chain mechanism. In addition to the homogeneous component of the process, which consists of three stages (chain initiation, prolongation, and rupture), in the presence of a catalyst there is also a heterogeneous component containing the same three stages. In the present work a theoretical evaluation was made of the change in the overall rate of hydrocarbon consumption (n-butane), i.e., the sum of all stages, resulting from changes in the concentration of active sites and initial hydrocarbon. The results help convey a qualitative picture of the role of hydrocarbon dilution on the rate of catalytic conversion. Thus, depending on the nature of the catalyst employed, the process may either be accelerated or inhibited by altering the energy and concentration spectrum of the hydrocarbon through dilution. Figures 4; references 3 (Russian).

UDC 541.128.3:546.98'74:[546.252.3-31+546.11]

Carbon Monoxide on Palladium Alloy Membrane Catalysts. Part I. Reaction of CO and H₂ on Binary Alloys of Palladium With Ruthenium and Nickel

18410035d Moscow KINETIKA I KATALIZ in Russian
Vol 29 No 4, Jul-Aug 88 (manuscript received
23 Jul 87) pp 850-871

[Article by O. S. Guryanova, Yu. M. Serov, S. G. Gulyanova, and V. M. Gryaznov, Friendship of Peoples University imeni Patrice Lumumba]

[Abstract] Synthesis based on carbon monoxide and hydrogen is attracting much attention both as a possible alternative hydrocarbon source and from an ecological standpoint. Broadening the choice of catalysts capable of engaging CO in various reactions will increase the range of products obtained by this means. This includes membrane catalysts that can radically affect the selectivity of a reaction and serve as a means for studying its mechanism. In the present work a study was made of the conversion of CO on binary palladium foils containing 10.0 percent Ru and 5.5 percent Ni in a stainless steel

reactor at 523- 683 K (at atmospheric pressure). Methane and ethylene formation along with carbon dioxide and water was observed, depending on how the hydrogen was introduced to the reaction zone. Positively charged hydrogen is absorbed on the surface of the catalyst and also enters the subsurface layer by solution. Both methods affect the selectivity and activities of the catalysts. References 5: 3 Russian, 2 Western.

Reaction of Carbon Monoxide With Oxygen in Adsorbed Layer on Pd, Ce, and Pd-Ce Catalysts on γ -Alumina Carrier

18410035e Moscow KINETIKA I KATALIZ in Russian Vol 29 No 4, Jul-Aug 88 (manuscript received 11 May 87) pp 866-871

[Article by G. S. Savelyeva, A. S. Sass, G. V. Speranskaya, K. K. Tenchev, L. A. Petrov, V. F. Vozdvizhenskiy, T. K. Galeev, and N. M. Popova, Organic Catalysis and Electrochemistry Institute, Alma-Ata]

[Abstract] Palladium and palladium-cerium catalysts on γ -alumina carriers are highly active in clearing waste gases of carbon monoxide and other harmful components. To better understand the mechanism of this activity, a study was made of the adsorption of the reacting components and the course of the oxidation of CO in the adsorbed layer by using Pd, Ce, and Pd-Ce catalysts. Thermal desorption, IR- spectroscopy, and differential scanning calorimetry showed that carbonate-carboxylate complex bridges are formed between CO and the carbon resulting from disproportionation and dissociation. These complexes then react with oxygen in the presence of Pd and Pd-Ce catalysts. Figures 4; references 13: 10 Russian, 3 Western.

Study of Iron-Ruthenium Systems by X-ray Photoelectronic Spectroscopy

18410035f Moscow KINETIKA I KATALIZ in Russian Vol 29 No 4, Jul-Aug 88 (manuscript received 19 Jan 87) pp 909-913

[Article by M. G. Chudinov, A. M. Alekseyev, D. M. Dmitrenko, V. M. Perov, and I. G. Nazarova, Nitrogen Industry and Products of Organic Synthesis State Scientific Research and Design Institute, Moscow]

[Abstract] Most industrial catalysts are multicomponent systems, and bimetallic systems are now being studied for certain chemical reactions. Extensive studies are being made of their physicochemical and especially their surface properties. It has been demonstrated that the surface composition of bimetallic systems differs markedly from their bulk composition. Experimental data obtained by photo- and Auger electron spectroscopy indicate that the upper-layer composition also depends on the conditions of treatment. Analysis of thermodynamic models of segregation surfaces shows that the catalytic properties depend heavily on the structure and composition of the surface. The surface of Fe-Ru systems, which are active in Fischer-Tropsch synthesis, was

found to be rich in Fe, while in another work it was demonstrated that Fe-Ru systems are also active in ammonia synthesis. Therefore, studying the surfaces of various Fe-Ru systems has become pressing. In the present work x-ray photoelectron spectroscopy was used to study the surfaces of oxidized, passivated, and reduced Fe-Ru as well as Fe-Ru-K systems. It was demonstrated that Fe and Ru are almost totally reduced at the surface and traces of Si, Na, S, Cl, and carbon and oxygen compounds were detected. The surfaces of reduced systems were found to be rich in Fe. The relative iron content on the surface of the Fe-Ru-K catalyst is two times greater than that on the surface of the industrial ammonia synthesis catalyst SA-1. Figures 3; references 15: 4 Russian, 11 Western.

UDC 541.128

Different Mechanisms and Kinetics of Oxidation of Sulfur Dioxide on Vanadium Catalysts

18410045b Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 61 No 9, Sep 88 (manuscript received 20 Mar 87) pp 1958-1964

[Article by S.V. Ivanenko]

[Abstract] Two mechanisms of the oxidation of SO_2 on vanadium catalysts were described and compared. One involves a description of the mechanism from the position of a 3-step stage-association mechanism according to which oxygen chemisorption on the active binuclear complex V_2O_4 with weakened V-O-V bonds forms an intermediate superoxide complex that later oxidizes the second SO_2 molecule without the direct participation of V_2O_5 oxygen. The other mechanism was derived by improving an associative mechanism that assumes the existence of a complicated complex, $\text{V}_2\text{O}_5 \cdot \text{xSO}_2 \cdot \text{xO}_2$, which forms at the second stage. SO_2 is not formed at the first stage of the mechanism, and instead of the superoxide complex, there is a peroxide complex with a different structure. Significant differences in these quite similar mechanisms were pointed out and discussed. The two mechanisms were also compared from the point of view of the kinetic equations derived from them. The equation best describing the entire aggregate of experimental data was singled out. Figure 1; references 21: 20 Russian; 1 Western.

UDC 541.12.03:546.562-31

Effect of Conditions of Preparation on Properties of Copper Oxide Deep Oxidation Catalysts

18410045c Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 61 No 9, Sep 88 (manuscript received 16 Mar 87) pp 1976-1980

[Article by L.A. Isupova, V.Yu. Aleksandrov, V.V. Popovskiy, and E.M. Moroz, Institute of Catalysis, USSR Academy of Sciences, Siberian Department]

[Abstract] An article examined the effect of preliminary mechanicochemical processing of the starting powder and the nature of the bonding agent on the physical and

chemical properties (strength, activity, and thermostability) of copper oxide deep oxidation catalysts. The copper oxide was prepared by the thermal decomposition of "pure" malachite in air at 673 K, followed by washing the sodium from the mixture up to a level of nearly 0.03 percent. Using the preliminary mechanicochemical processing described or introducing a glue consisting of aluminum hydroxy-nitrate made it possible to prepare a molded catalyst from the copper oxide powder. The increase in the strength of the catalyst granules that occurs when the duration of mechanicochemical activation is increased or after the aluminum hydroxy-nitrate solution is introduced increased the strength of the single contact. The reduction in the catalytic activity that occurred after gluing by the aluminum hydroxy-nitrate solution ensued primarily from blockage of part of the active centers on the CuO surface, which was associated with the dislocations' rise to the surface. The decrease in catalytic activity that occurred when the calcination temperature was increased to 937 K was attributed to the sintering of crystallites and to a decrease in the number of active centers. The introduction of aluminum oxide produced a thermostabilizing effect. A catalyst containing up to 10 percent aluminum oxide, which was produced by preliminary mechanicochemical processing and subsequent gluing, was found to be the optimum copper oxide catalyst. Figure 1; references 13: 12 Russian; 1 Western.

UDC 665.644.44

**Improving Catalytic Properties of
Aluminoplatinum Reforming Catalysts by
Modifying Organometallosiloxanes**

18410045d Leningrad ZHURNAL PRIKLADNOY
KHIMII in Russian Vol 61 No 9, Sep 88 (manuscript
received 21 Jan 87) pp 2046-2051

[Article by A. P. Fedorov, S. G. Gorlov, I. M. Kolesnikov, N. M. Belov, Ye. A. Shkuratova, B. F. Gulev, and M. S. Grigoryev, Branch of Lenneftekhimp Scientific Production Association]

[Abstract] A study examined the catalytic properties of an aluminoplatinum catalyst that had been modified by silicon organic compounds in reforming reactions that characterize the activity of its metallic and acid functions. Metallophenylsiloxanes having the general formula $(\text{MeO}_x\text{x}[\text{Si}(\text{OH})_n\text{xR}_m])_x$ and containing tin or cobalt and tungsten were used. Treating the surface of

the aluminoplatinum reforming catalysts with a small quantity of such compounds improved their most important operational properties: activity, selectivity, and stability. The best catalytic properties were found in samples synthesized by introducing a tin-containing modifier into the catalysts after applying platinum to the $\gamma\text{-Al}_2\text{O}_3$ surface. By using Mossbauer spectroscopy it was possible to discover that the active state of tin in the catalysts is found predominantly in the bivalent state. Figures 4; references 6 (Russian).

UDC 66.094.373

**Physicochemical Study of Silver Catalysts of
Oxidative Dehydrogenation of Methanol**

18410045e Leningrad ZHURNAL PRIKLADNOY
KHIMII in Russian Vol 61 No 9, Sep 88 (manuscript
received 14 Jul 86) pp 2051-2055

[Article by S. P. Noskova, A. A. Davydov, A. N. Pestryakov, G. I. Goldenberg, and T. K. Popova, Institute of Catalysis, USSR Academy of Sciences, Siberian Department]

[Abstract] Some commercial plants use "silver on pumice" as a catalyst of formaldehyde production while others use "silver on aluminosilicate." These compounds were studied because, while their properties differ considerably, their activity and selectivity are similar. Samples of pumice from different localities and synthetic aluminosilicate were used as carriers, and their properties were presented in a table and discussed. In spite of the different textural characteristics of the aluminosilicate and pumice used, common regularities of the formation of the active component during the preparation of "silver on aluminosilicate" and "silver on pumice" catalysts were found. In both cases, part of the silver introduced was concentrated on the surface of the catalyst granules, and a porous crust or relatively compact metal layer formed. Another part of the silver is present in the form of $\text{Ag}^{\delta+n}$ ($1 < n < 7$) type of clusters. A specific feature of the "silver on aluminosilicate" catalyst is that it results in a transformation of the structure of the original carriers. This is due to fusions of the active component that block a considerable part of the silver introduced into the carrier matrix. Figures 2; references 10; 7 Russian; 3 Western.

UDC 546.77-145.03

Anode Dissolution of Molybdenum in Ammonium Sulfate Solutions Containing Hydrogen Peroxide
18410011b Tashkent *UZBEKSKIY KHIMICHESKIY ZHURNAL* in Russian No 3, May-Jun 88 (manuscript received 28 Dec 87) pp 6-9

[Article by G. A. Tsyganov, S. Tukhtayev, T. Artykbayev, and Sh. U. Ganiyev, Chemistry Institute, Tashkent]

[Abstract] Anode oxidation of molybdenum in acid and alkaline media occurs through an oxide layer, and the passivation that occurs during this process imparts certain specifics to the electrochemical behavior of this metal. It is likely that the surface of the metal becomes covered with this layer as a result of the relatively low reaction rate of the electrolyte components with these oxides as compared with the formation of the latter on the surface of the electrode during anode oxidation. To accelerate the reaction, a component such as hydrogen peroxide, which can react vigorously with the molybdenum oxides, must be added to the electrolyte. In the present work a study was made of the behavior of the anode dissolution of molybdenum in an electrolyte containing from 1 to 7.5 g/L ammonium sulfate and 50 g/L hydrogen peroxide at various current densities at 30°C. It was demonstrated that when the component concentration in the electrolyte remains constant the quantity of molybdenum in solution increases in direct proportion to the increase in current density. On the other hand, increasing the content of ammonium sulfate at a

constant current density lowers both the intensity of metal dissolution and the catalytic decomposition of hydrogen peroxide per unit of time. Figures 4; references 5 (Russian).

UDC 542.61:546.91

Extraction of Noble Metals With Surfactants
18410011c Tashkent *UZBEKSKIY KHIMICHESKIY ZHURNAL* in Russian No 3, May-Jun 88 (manuscript received 28 Dec 87) pp 9-11

[Article by A. G. Ganiyev, R. N. Gafurova, M. K. Yuldasheva, N. A. Khodzhakhanov, M. Ernazarov, and Kh. R. Rakhimov, Chemistry Institute, UzSSR Academy of Sciences]

[Abstract] During extraction from alkaline, sulfuric acid, and weak hydrochloric acid solutions with slightly water soluble quaternary ammonium bases (dimethylbenzylalkylammonium chlorides, diethylbenzylalkylammonium chloride) in 1,2-dichloroethane and butyl or isoamyl alcohols, platinum and gold are separated from other nonnoble metals as well as rubidium, radium, and iridium. All of the aforementioned surfactants are derived from costly and scarce stocks, and they are selective for only one or two elements. It is thus necessary to search for new, less costly, and more available reagents such as alkylaryliothiuronium chlorides (AAITKh-M), which have surfactant properties and are oil-soluble salts of a quaternary ammonium base synthesized from the bottoms stock remaining after the phenol refining of petroleum. Noble metals coexist with other elements such as copper, iron, nickel, cobalt, antimony, and arsenic. For this reason, radioactive tracers of these elements were used to study the extraction of noble metals with the AAITKh-M cation. Optimum conditions were determined, and the possibility of extracting osmium, rubidium, and silver from acid and alkaline solutions was established. Figures 4; references 4: 3 Russian, 1 Western.

UDC 541.124.13

Kinetics of Energy Evolution During High Temperature Ignition of Hydrocarbon Mixtures with Air and Oxygen

18410351b Moscow *KHIMICHESKAYA FIZIKA* in Russian Vol 7 No 5, May 88 (manuscript received 29 Apr 87) pp 665- 673

[Article by A. A. Borisov, V. M. Zamanskiy, V. V. Lisyanskiy, G. I. Skachkov, K. Ya. Troshin, and I. M. Baranov, Chemical Physics Institute, Moscow]

[Abstract] When conducting studies on autoignition processes the time delay T_i (induction period) preceding ignition is normally assumed to be much greater than explosion time, T_e . This is justifiable for cases of high activation energy, and also for processes taking place at low temperatures. In this case the total time of heat evolution, T_i plus T_e , actually consists of T_i and T_e may be neglected. Much experimental data accumulated under static conditions at adiabatic compression in shock tubes at 900- 1500 K and pressures not exceeding several atmospheres indicate that T_i is at least several times greater than T_e . However, data obtained in shock tubes show that at sufficiently high temperatures, the relationship between the two can be reversed, and that the kinetics of heat evolution in an exothermal reaction may be dissimilar to a conventional thermal or chain-thermal explosion. During detonation the heat evolution process follows the rules of adiabatic autoignition and reaction kinetics becomes one of the major factors determining collapse of detonation waves at the combustion-detonation threshold. It is thus necessary to analyze the extent to which the reactions beyond detonation wave front correspond to chain-thermal explosion. Furthermore, detonation wave stability and their structure cannot be resolved solely on the basis of ignition delay data, without knowing the basic kinetics of heat evolution as a whole. In the present work a study was made of the time characteristics of heat evolution in hydrocarbon mixtures with air and argon at 1250- 1700 K and pressures of 0.6-8 atmospheres beyond reflected shock waves. Relationships were determined for T_e and T_i as functions of pressure, temperature, composition, and presence or lack of a promoter. Extrapolation of the data to the high pressures (30 atm) characteristic for detonation of hydrocarbon mixtures, shows that within the concentration limits of detonation, T_i is considerably greater than T_e , and that the latter determines the course of the reaction. A formula for calculating reaction rate over a broad temperature range is presented. Figures 7; references 14: 9 Russian, 5 Western.

UDC536.46

Theory of Nonstationary Combustion of Condensed Systems Taking Time Delay into Consideration

18410351c Moscow *KHIMICHESKAYA FIZIKA* in Russian Vol 7 No 5, May 88 (manuscript received 12 Jun 87) pp 674- 687

[Article by B.V. Novozhilov, Chemical Physics Institute, Moscow]

[Abstract] A new approximation in the theory of nonstationary combustion in condensed systems makes it possible to take into consideration the time lag of the

chemical conversion zone and the heat regions of the gas and combustion products. It is named the t_r -approximation to distinguish it from the t_c - approximation which accounts only for the time lag of the heated layer of the condensed phase as currently used in the theory of nonstationary combustion. In this new approximation, nonstationary phenomena can be investigated using the properties of the stationary modes of combustion. The role of time lag zones is brought in as a time differential, i.e. a phenomenological quantity. A previously proposed model of combustion, and another example of time lag within the reaction zone of a condensed phase, both capable of analytical solution, are used to demonstrate the effectiveness of the new approximation. References 18 (Russian).

UDC662.215.4

Effect of Loading Rate on Parameters of Breakdown and Ignition of Thin Layers of Solid Fuel Particles

18410351d Moscow *KHIMICHESKAYA FIZIKA* in Russian Vol 7 No 5, May 88 (manuscript received 15 May 87) pp 688- 693

[Article by Ye. A. Avdeyev and A. V. Dubovik, Chemical Physics Institute, Moscow]

[Abstract] Research on the rules governing ignition of solid fuels during impact shows that both the critical parameters of the process (pressure and thickness of the charge) and the effective rigidity limits of the solid fuel are independent of loading rate within a range up to 5 meters per second. This fact has been explained within the framework of models of spontaneous disintegration of solid fuel samples valid after flashing. However, as the load rate is increased and high values of pressure rate increase are realized, changes in the critical parameters of initiation may be expected. It has been demonstrated that heating during disintegration of solid fuel pellets under impact is a function of the heating time T_r and rate of the contacting surface of the impacting machine w . The quantity T_r can be determined from the circulation time of sound waves in the loading system. In the present work a general method is proposed for computing w which is applicable for "friable" substances in impact-mechanical interactions having an arbitrary loading profile. Samples of octogen, hexogen, and TENA were subjected to impacting at loading rates of 4.4 and 25 meters per second for charges 19 mm in diameter. It was demonstrated that increasing the loading rate results in an increase in critical thickness and effective rigidity limits of the samples. Critical pressure increased with TEN and decreased with octogen and hexagen. The results are explained within the framework of known solid fuel ignition models during mechanical interaction. Figures 4; references 8 (Russian).

UDC 543.311

Acid Rain in Estonian SSR. 3. Variation in Rain Characteristics With Wind Direction in Tallin

18410033 Tallin IZVESTIYA AKADEMII NAUK
ESTONSKOY SSR: KHIMIYA in Russian
No 3 Jul-Sep 88 (manuscript received
30 Dec 87) pp 210-214

[Article by Aade Lemmik and P. Luyga, Institute of Chemistry, Estonian Academy of Sciences]

[Abstract] This article compares the results of the analysis of liquid precipitation in 1983-1986 in two regions of Tallin and discusses the variation in the major characteristics of precipitation with wind direction. Samples were collected simultaneously at the two points when possible or individually if rain was only falling in one of the two regions. In addition to the expected variation in rain composition caused by industrial sources of dust, sulfates, and other components, there was an unexpectedly high content of chlorides in rain falling with winds from the South and Southeast, directions in which there are no industrial sources of chlorides. It is assumed that the unknown source is agricultural. The studies indicate that the pollution of the air in Tallin results largely from local sources of emission and vehicular transport. Interactions of various types of ingredients such as the reaction of gaseous acid components with dust play a significant role. Figures 4, references 4: 2 Russian, 2 Eastern European.

UDC 614.72

Detoxification of Coke Chemical Off-Gases

18410041f Kiev KHIMICHESKAYA TEKHOLOGIYA
in Russian No 5, Sep-Oct 88 (manuscript received
13 Dec 87) pp 69-71

[Article by V. G. Kulbachnyy and Ye. S. Dubinskaya, Gas Institute, Kiev]

[Abstract] The known methods for treating off-gases at coal tar and oil refineries fail to provide complete elimination of toxic components. Catalytic afterburners become clogged with carbon, while heat treatment of polycyclics, which is effective only at temperatures greater than 1,300°C, forms oxides of nitrogen that are no less toxic than the organic impurities are themselves. The present work presents a new method for detoxifying polycyclic aromatic hydrocarbons in which the thermochemical, thermal, and catalytic stages are combined. The preliminary thermochemical treatment circumvents the formation of nitrogen oxides and carbonization of the catalyst. The process is based on controlling the air intake to provide a molecular hydrogen-rich atmosphere

that converts the heavy hydrocarbons into lower-molecular hydrocarbons and carbon dioxide. The method is said to provide a 99.5 percent purification. References 12: 11 Russian, 1 Western.

UDC 630*86:628.543

Wastewater Treatment with Prolonged Aeration at Low Temperatures

18410057a Moscow GIDROLIZNAYA I
LESOKHIMICHESKAYA PROMYSHLENNOST in
Russian No 9, Sep-Oct 88 pp 9-11

[Article by L. I. Kornilov and Ye. M. Kryuchikhin, Specialized Regulatory Environmental Protection Administration, All-Union Scientific Industrial Association of the Cellulose and Paper Industry, and V. I. Siplivkyh, Neyvo-Rudyanka Wood Chemical Plant]

[Abstract] Wastewater treatment at the Neyvo-Rudyanka Wood Chemical Plant is complicated by the low temperatures that are prevalent during much of the year and by the fact that, although relatively new, the technology itself is basically 20 years old. An analysis of the factors important in secondary treatment involving aeration and activated sludge demonstrated that biological purification still continued at low temperatures on the order of 8 to 11 degrees C, albeit at a decelerated pace. For a 6-month period—October through March—monitoring studies confirmed the effectiveness of a process with prolonged aeration (45 to 50 h), low sludge load (60 to 100 g/(g x day)), and dissolved oxygen levels of 6 g/m³. The rate of endogenous respiration in that temperature range was on the order of 2-3 percent of sludge weight per day. With additional filtration and storage in an aerated pond, the treated water had a BOD of 5-8 g/m³, 3-6 g/m³ suspended solids, and 8-9 g/m³ dissolved oxygen. References 9 (Russian).

UDC628.349:661.666.2

Coquina Used to Treat Chromium and Iron Bearing Industrial Sulfate Effluents

18410131f Kiev KHIMICHESKAYA TEKHOLOGIYA
in Russian No 1, Jan-Feb 89 (manuscript received
25 Mar 87) pp 93-96

[Article by V. P. Goncharik, I. G. Chernysh, and L.I. Kozhara, Surface Chemistry Institute, Kiev]

[Abstract] Treatment of effluents containing chromium and iron sulfates normally includes neutralization of the sulfuric acid and precipitation of the metal ions with various alkaline reagents such as oxides, hydroxides, and carbonates of alkali and alkaline earth metals, especially caustic soda and lime, and various liquid and solid alkaline industrial wastes. Another promising neutralizing agent is coquina, a sedimentary calcium carbonate, especially the low cost tailings. In the present work a study was made of the effects of coquina quantity and particle size, concentrations of sulfuric acid and iron and

chromium salts, and mixing time on the extent of neutralization of the effluent. Tests showed that most of the sulfuric acid is neutralized within the first 15 minutes, after which the process slows down. It may be

accelerated by using a more basic reagent such as sodium carbonate. Two possible methods for treating effluents with coquina are recommended. Figures 3; references 10: 5 Russian, 5 Western.

UDC 543.8

Potentiometric Determination of Total Dicarboxylic Acids in Ammophos

18410011a Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 3, May-Jun 88 (manuscript received 28 Dec 87) pp 3-5

[Article by S. S. Ishankhodzhayev, A. Kh. Narkhodzhayev, and S. Tukhtayev, Chemistry Institute, Tashkent]

[Abstract] Agrochemical research has proved that the efficiency of mineral fertilizers may be increased by adding physiologically active substances such as dicarboxylic acids. During the production of ammophos fertilizers it is necessary to control the content of dicarboxylic acids (succinic, glutaric, adipic, etc.) in the end product. In the present work a method was developed for determining the total dicarboxylic acid content in ammophos in nonaqueous media. The ammophos samples contain sesquioxide phosphates and other impurities in addition to ammonium phosphate. These impurities interfere with the titration of dicarboxylic acids in aqueous or aqueous acetone solutions. The current titrimetric method is based on measuring the potential differences between two electrodes at low current strength with an EV-74 universal ionmeter. The titrating agent used was 0.01 N KOH in predistilled ethyl alcohol. Between 40 and 45 minutes was required for the analysis, and the error amounted to 2.0 percent by weight. Figure 1; references 9 (Russian).

UDC 631.811'84'85

Manganese-Containing Ammophos From Karatau Phosphorites

18410011d Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 3, May-Jun 88 (manuscript received 29 Jan 88) pp 59-60

[Article by O. M. Makhmadmuradov, Ye. A. Buslayev, M. A. Mukhamedzhanov, A. M. Amirova, S. M. Tadzhiyev, and L. S. Rustamova, Novokokand Chemical Plant, Chemistry Institute, UzSSR Academy of Sciences]

[Abstract] Combining trace element salts with basic fertilizers in a single technological process is both economical and ecologically sound. Adding manganese

salts to the phosphoric acid extractant during the ammoniation process at pH values above 3.2 results in the formation of monohydrated manganese hydrophosphate. Manganese ammonium phosphate monohydrate becomes present in the solid phase of the slurry at pH 4.0. However, up to 78 percent of the added manganese is contained in the water-insoluble form, and at pH 5.8 almost all of the manganese (99.5 percent) is transformed into citrate-soluble compounds. At the Novokokand Chemical Plant an experimental lot of manganese-containing ammophos was produced from manganese nitrate hexahydrate containing 19 percent Mn. The product was dissolved in crystal hydrate water at 40 to 50°C and metered into the ammophos slurry. About 90 percent of the total manganese is in the assimilatable form, and about 14 percent of that amount is water soluble. The resulting ammophos is similar to conventional ammophos. It resulted in a 3.0 to 3.5 centners per hectare increase in production when used on cotton fields. Its effect on cotton quality is being studied.

UDC 631:811.631+577.17.049

Effectiveness of Nitrogen Fertilizers Containing Trace Elements (Zn and Mo)

18410044H Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 4 Jul-Aug 88 (manuscript received 25 Jan 88) pp 78-79

[Article by Kh. Kh. Khaitbayev and A. T. Aliyev, Institute of Chemistry, UzSSR Academy of Sciences]

[Abstract] Experiments were performed in typical sierozems with a low zinc and molybdenum content. Nitrogen fertilizers containing zinc and molybdenum (0.2 and 0.1 percent of the mass of pure nitrogen, respectively) were synthesized. The nitrogen and phosphorus utilization factors were increased by 8-12 and 8-10 percent when these fertilizers were used. The effectiveness of the trace elements depends on the type of cotton on which the fertilizer is used. References 2: Russian.

UDC 541.124-16:663.3.7

Sintering of Barium Titanate. Part II. Structure and Electrophysical Characteristics of Ceramics Made of Nonuniform Powders

18410010a Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKIYE NAUKI No 4, Jul 88 (manuscript received 11 Apr 86) pp 27-31

[Article by V. F. Sysoyev and V. V. Zyryanov, Solid-State Chemistry and Minerals Refining Institute, Siberian Department, USSR Academy of Sciences, Novosibirsk]

[Abstract] In a previous work, the nonuniformity of the initial powder was shown to have a great effect on the sintering kinetics and final porosity of sintered ceramics. The present work studies the structures of sintered ceramics made from powders by wet milling in a ball mill (containing particles smaller than 5 μm), by dry milling in a planetary-centrifugal mill (containing dense clumps to 30 μm and nonmilled particles of 1 μm), and by air-centrifuge particle size sorting (containing particles and aggregates smaller than 5 μm). The ceramics's structure was determined by using a scanning electron microscope to analyze ceramic chips obtained after cooling in liquid nitrogen. Depending on the method used to mill the initial powder, the structure of the sintered ceramic was found to be of three types: 1) that resulting from a ceramic sintered from relatively uniform and coarse powders (wet milling), 2) that sintered from highly nonuniform powders obtained by dry milling in a planetary-centrifugal mill, and 3) a ceramic sintered from fines. Particle size and porosity varied extensively in all three structures, especially in structures 1 and 2. The results demonstrate that, in addition to the well-known and widely used methods of controlling sintering by using additives, the final properties of a ceramic may also be controlled by its structure as determined by the method of preparing the initial powder. Dry milling in a planetary-centrifugal mill lined with the same material and subsequent sorting makes it possible to prepare a barium titanate ceramic having good dielectric properties. Figures 3; references 9: 4 Russian, 5 Western.

UDC 541.135.4+546.46.11

Conductivity of Magnesium Hydride

1841010b Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKIYE NAUKI No 4, Jul 88 (manuscript received 24 Jun 86) pp 41-44

[Article by N. F. Uvarov, K. B. Gerasimov, and Ye. Yu. Ivanov, Solid-State Chemistry and Minerals Refining Institute, Siberian Department, USSR Academy of Sciences, Novosibirsk]

[Abstract] Research on the physical properties of magnesium hydride centers around the possibility of using it as a low-cost rechargeable hydrogen battery. To evaluate

the reaction kinetics of magnesium hydrogenation and magnesium hydride dehydrogenation, information is needed on the auto-diffusion of the hydride ion. This may be obtained by measuring conductivity. The conductivity of magnesium hydride has never been studied before. In the present work a study was made of the types and temperature dependency of magnesium hydride electrical conductivity. Freshly prepared magnesium hydride was compressed into a pellet, and one surface was coated with fine platinum. The other surface was coated with metallic magnesium. Conductivity, volt-ampere characteristics, and emf were measured at various temperatures and hydrogen pressures in a specially prepared cell. Current was found to be transmitted in magnesium hydride through ionic defects in the hydride ion sublattice. The apparently low rate of hydrogenation of magnesium, after the formation of a protective hydride film, is related to the low transfer rate of electrons from magnesium to adsorbed hydrogen. Therefore, to increase the magnesium-to-hydride conversion rate after formation of the protective film, it is necessary to create electronic (not ionic) defects in the magnesium hydride lattice, i.e. to somehow increase the electrical conductivity of the magnesium hydride. Figures 3; references 9: 2 Russian, 7 Western.

UDC 548.4

Thermodynamic Analysis of Effect of Isovalent Doping on Equilibrium of Indigenous Point Defects in Gallium Arsenide

18410019a Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 57 No 7, Jul 88 (manuscript received 15 Jul 87) pp 1764-1770

[Article by R. Kh. Akchurin, Fine Chemical Technology Institute imeni M. V. Lomonosov, Moscow]

[Abstract] The effect of isovalent admixtures on the properties of a semiconductor is manifested in the change in the totality of point defects present in the crystal lattice of the semiconductor. The processes causing these changes could include both the solid-state interaction between indigenous and admixture atoms (which are capable of altering the composition and content of various complexes as a result of the point defects of the admixed and indigenous atoms) and their direct interaction in the crystallization medium (which could cause changes in the equilibrium concentration of various types of point defects in the crystallized material). Significant differences in the concentration of indigenous point defects in gallium arsenide samples crystallized at the same temperature indicate that a change in component activity in two-component solution-melts could have a considerable effect on shifting transitory equilibrium between various types of defects in the equilibrium solid phase. A similar interaction may be effected by introducing supplemental elements into the melt to cause a change in the activities of the basic components of the compound. In this case, the introduced element must be isovalent in nature to exclude the

possibility of its having a direct effect on the properties of the crystallized compound due to alloying. An estimate of the possible limitations in changes in defect composition of doped gallium arsenide crystals resulting from isovalent element admixtures thus becomes interesting. In the present work such an estimate is made on the basis of gallium arsenide doped with indium and antimony. Equilibrium constants of quasichemical reactions describing the formation of indigenous point defects during crystallization of GaAs(In) and GaAs(Sb) were determined, and the concentrations of Ga and As vacancies were calculated. Concentration changes in point defects as a function of temperature and degree of doping were analyzed. Figures 3; references 7: 6 Russian, 1 Western.

UDC 536.722'63+546.271'657'659'662

Thermodynamic Properties of Monocrystalline Hexaborides of Neodymium, Samarium, and Gadolinium Over Broad Temperature Range
18410019b Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 57 No 7, Jul 88 (manuscript received 21 Jul 87) pp 1771-1775

[Article by A. S. Bolgar and V. B. Muratov, Problems of Materials Science Institute, Kiev, UkSSR Academy of Sciences]

[Abstract] Hexaborides of rare earth metals are used in many branches of modern technology as a result of their many interesting physical properties. These metals may also be considered as models for clarifying the effects of monotonic filling with electrons of the f-shell of rare earth metal atoms on the level of the thermodynamic properties of these metals. A systematic study of the thermodynamic characteristics of rare earth metal hexaborides over a wide temperature range has never been done. In the present work the enthalpies of neodymium, samarium, and gadolinium hexaborides have been determined at 400-2300 K, and the temperature variations of enthalpy, heat capacity, entropy, and Gibb's energy were calculated. The high values of the experimentally determined heat capacities of hexaborides formed from rare earth metals having some unfilled f-shells may be due to the possibility of electron transfers from tightly packed f-shells to the zone of conductance and growth as a result of this electron-created heat capacity. This is confirmed by the marked drop in electrical resistance of samarium hexaboride single crystals with increasing temperature. References 16: 15 Russian, 1 Western.

UDC 541.141

Laser Chemical Structuring of Vinyl Monomers by Complex Formation With 3d-Metal Acrylates
18410037A Kiev *UKRAINSKIY KHIMICHESKIY ZHURNAL* in Russian Vol 54 No 9 Sep 88 (manuscript received 27 Jun 86) pp 899-903

[Article by S. V. Volkov, A. V. Botsman, V. I. Lutoshkin, and A. D. Pomogaylo, Institute of General and Inorganic Chemistry, Ukrainian Academy of Sciences, Kiev]

[Abstract] The purpose of this work was to estimate the structuring effect of cobalt, nickel, and copper acrylates

in gelatin layers under the influence of monochromatic laser radiation at 633 nm. The basic composition consisted of a macromolecular ligand or matrix, i.e., gelatin, a sensitizer, i.e., methylene blue, and a reducing agent, i.e., triethanolamine. For the first time 3d-metal acrylates were used as the cross-linking and structuring agents. IR spectroscopy and electron absorption spectroscopy were used to analyze the aqueous 3d-metal acrylate solutions, then the gelatin films treated with these metal acrylates, and then the same films after dehydration. Analysis of the IR spectra is used to suggest a photochemical structuring plan for the macrocomplexes. The photoprocesses occurring are oxidation-reduction reactions requiring the ability of the dye excited by light to be converted to a semiquinone reacting with the monomer. An overall scheme is suggested for the conversions occurring. Figures 3, references 12: 9 Russian, 3 Western.

UDC 546.712'722'742+543.226+548.743.3

Coprecipitation and Crystallization of Yttrium and Zirconium Hydroxocarbonates
18410037B Kiev *UKRAINSKIY KHIMICHESKIY ZHURNAL* in Russian Vol 54 No 9 Sep 88 (Manuscript received 11 Jun 87) pp 912-915

[Article by S. A. Nedilko, G. V. Panchenko, N. P. Shpakovskaya, and V. A. Dubok, Kiev University; Institute of Materials Science Problems, Ukrainian Academy of Sciences, Kiev]

[Abstract] A study examined the conditions of the coprecipitation of hydroxides and carbonates of zirconium and yttrium from aqueous solutions of their salts as well as their composition, properties, and transformations during drying and heating processes. The variation of zirconium and yttrium hydroxocarbonate coprecipitation with the type and quantity of precipitant and the acidity of media were studied. The influence of organic additives on the process of the coprecipitation of these metals and on the formation of solid solutions based on zirconium dioxide from coprecipitated hydroxocarbonates was also studied. In specimens held at 300°C, a cubic phase began to form. At 300-575°C the cubic phase predominated, and a tetragonal phase appeared, while at 575-800° the major phase was monoclinic with tetragonal and cubic impurities. Figures 3, references 12: 8 Russian, 3 Western.

UDC537.312.62

Features of Magnetic and Elastic Properties of Superconductor Type YBa₂Cu₃O_{7-δ}, Altered by Crystal Structure Defects
18410351a Moscow *KHIMICHESKAYA FIZIKA* in Russian Vol 7 No 5, May 88 (manuscript received 20 Jul 87) pp 579-584

[Article by L. G. Mamsurova, K.Sj. Pigalskiy, Yu. D. Tretyakov, N. G. Trusevich, and L. G. Shcherbakova, Chemical Physics Institute, Moscow]

[Abstract] A study was made of magnetic permeability and magnetization as functions of temperature and field

strength (to 60 kilo-Oersteds), as well as the relationship between Young's Modulus and internal friction (as calculated by measuring longitudinal sound velocity at 160 kHz) within the temperature range 4.2-300 K of the title compounds prepared by various methods. Phase composition of ceramics prepared cryogenically was controlled by X-ray diffraction diagrams. The experiments demonstrate that the magnetic and elastic properties of these compounds are largely due to the presence of structural defects and pores. The modulus of elasticity changes in a nonmonotonous manner as temperature is reduced below room temperature and is characterized by the

existence of anomalies above and below the superconductivity transition temperature. A significant increase in acoustic loss was also observed at the same temperature interval. The observed anomalies are evidently due to the crystal structure of the compounds, especially structural defects in both the anionic and cationic sublattices. The data were correlated with changes in magnetic properties (irreversibility of magnetization curves and the appearance of a frozen current on removal of the magnetic field) which are also caused by defects in the compounds, acting as effective pinning sites. Figures 6; references 3: 2 Russian, 1 Western.

UDC 547.241

**Bromoacetylenephosphonate as Dienophile in
Diels-Alder Reaction**

18410012p Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 25 Dec 87) pp 1662-1663

[Article by A. I. Senderikhin, A. V. Dogadina, B. I. Ionin,
and A. A. Petrov, Technological Institute imeni Lens-
ovet, Leningrad]

[Abstract] Although acetylenephosphonates are dienophiles, only a few have been used in Diels-Alder reactions, chiefly those containing an additional acceptor group. In the present work it was demonstrated that dimethylbromoacetylenephosphonate, which is prepared by reacting dibromoacetylene with trimethylphosphite, is also an active dienophile that can be used to prepare derivatives of bromine-substituted carbocyclic phosphonic acids. Specifically, 2,3-dimethyl-1,3-butadiene was heated with dimethylbromoacetylenephosphonate to form the dimethyl ester of 2-bromo-4,5-cyclohexadienephosphonic acid. References 5: 1 Russian, 4 Western.

UDC 543.24

**Analysis of Polymer Metal Complexes With
Different Metals Based on Copolymer of
N-Vinylpyrrolidone With Crotonic Aldehyde**

18410044f Tashkent *UZBEKSKIY KHIMICHESKIY
ZHURNAL* in Russian No 4 Jul-Aug 88 (manuscript
received 25 Jan 88) pp 43-46

[Article by Sh. T. Mamadaliyev, Ye. V. Zimakova, and
U. M. Mirzayev, Institute of Chemistry and Physics of
Polymers, UzSSR Academy of Sciences]

[Abstract] A study examined the influence of the polymer base of a specimen of N-vinylpyrrolidone—crotonic aldehyde (VP-CA) copolymer by direct complexometric titration with xylene orange in model solutions. It was found that a 1,000-fold excess of VP-CA did not influence the determination of the metal ions present. Ions of cobalt, copper, zinc, and manganese can thus be determined without removing the VP-CA polymer matrix, thereby significantly speeding up the process of determining metal ions in the compounds. The determination of cobalt, copper, zinc, and manganese is described. The method is distinguished by the simplicity of the apparatus required and by its good accuracy. References 6: Russian.

Quantum Chemical Study of Phosphoryl Amide Group in Phosphorylammonium Cationites and Phosphorylazolides of Phosphoric Acid Diesters
18410010d Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKIYE NAUKI No 4, Jul 88 (manuscript received 10 Apr 87) pp 111-117

[Article by T. V. Maltseva, L. N. Shchegoleva, I. K. Korobeynischeva, and Ye. M. Ivanova, Novosibirsk Organic Chemistry Institute, Novosibirsk Bioorganic Chemistry Institute, Siberian Department USSR Academy of Sciences]

[Abstract] The reaction of phosphoric acid diesters with alcohols in the presence of condensing agents is accelerated by nucleophilic catalysis of heterocyclic amines resulting from the formation of highly labile intermediates, phosphorylazolides (I), or phosphorylammonium cations (II). It has been demonstrated that in tertiary amines such as pyridines and N-substituted imidazoles the catalytic effect in the formation of phosphorus triesters is a function of the concentration and the relative stability of the intermediate compounds formed during the course of the reaction, i.e. the greater the stability, the more the equilibrium is shifted toward the side of product formation. For compounds such as I and II, variances have been observed in the frequencies of valence oscillations of the phosphoryl group and its NMR chemical shift. These variances have been ascribed to structural features of the phosphorylamide group and could possibly have an effect on the catalytic activity of amines. In the present work quantum chemical calculations with a Viking program were made to clarify the relationship between the above frequencies and NMR chemical shifts for active derivatives of compounds I and II. The results indicate that the Waiberg index (P-N) makes it possible to predict the relative stability of active derivatives and thereby evaluate the catalytic effect of heterocyclic amines with nitrogen atoms of the pyridine type. Figure 1; references 7: 4 Russian, 3 Western.

UDC 547.341:548.737

Molecular Structure and Hydrolysis of 2-Alkoxy-2-oxo-3H-1,4,2- benzodioxaphosphorines
18410012a Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript received 16 Dec 86) pp 1456-1461

[Article by A. N. Chekhlov, V. N. Solovyev, G. F. Makhayeva, V. L. Yankovskaya, A. N. Bovin, A. N. Degtyarev, Ye. N. Tsvetkov, and I. V. Marshynov, Physiologically Active Substances Institute, Chernogolovka]

[Abstract] In a previous work the title compounds were found to respond readily to hydrolysis and alcoholysis, rupturing the endocyclic O-P bond. The unusually low hydrolytic stability of these compounds prompted a comparison of their hydrolysis reaction rate constants

with those of a structural isomer, 2-oxo-4H-1,3,2- benzodioxaphosphorine, whose properties as pesticides (saligenin cyclophosphates and their analogues) are widely acknowledged. Hydrolysis was studied potentiometrically at a constant pH under conditions close to those reported for the isomers. The monomolecular hydrolysis reaction rate constants for the title compounds were determined to be from 1 to 3 orders of magnitude less than those of the isomers. An X-ray structural analysis of 2-ethoxy-2-oxo-3-phenyl-3H-1,4,2- benzodioxaphosphorine indicates that the observed enhanced inclination to hydrolysis is due to differences in geometric structure. Figure 1; references 10: 6 Russian, 4 Western.

UDC 546.185+547.241

Trichloromethanephosphonic Acid Amides
18410012b Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript received 16 Dec 86) pp 1461-1468

[Article by G. N. Koydan, A. P. Marchenko, V. A. Oleynik, and A. M. Pinchuk, Organic Chemistry Institute, Kiev]

[Abstract] The complete amides of trichloromethanephosphonic acid were unknown until quite recently. This was apparently due to their chemical properties, which made it difficult to isolate them. Compounds of this type were first prepared in 1984 by reacting trichloromethyl-dichlorophosphine with excess dialkylamine in ether. Interest in these compounds centers on the proximity of the trichloromethyl and amidophosphoric functions in one molecule, which enables them to react with halogen-containing compounds. In the present work NMR spectra were used to demonstrate that the rearrangement of tetraalkyldiamidotrichloromethanephosphonites into P-Cl-ilides is accelerated with the addition of tetraalkyldiamidotrichloromethylchlorophosphonic chloride, chlorine, oxygen, or sulfur, while liquid ammonia or tert-butyl amine inhibits the reaction. References 9: 8 Russian, 1 Western.

UDC 542.91:547.1'118

Method for Preparing Phosphorylated Derivatives of 1,6-Dibromo-1,6- dideoxy-D-mannite
18410012o Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript received 3 Jul 87) pp 1661-1662

[Article by L. I. Gurariy, O. K. Pozdeyev, G. Kh. Gilmanova, E. T. Mukmenev, and B. A. Arbuzov, Organic and Physical Chemistry Institute imeni A. Ye. Arbuzov, Kazan]

[Abstract] The known capability of 2,7,8-trioxa-1-phosphabicyclo[3.2.1]octanes to convert in the presence of halogens into 2-halo-4-halomethyl-2-oxo-1,3,2-dioxaphosphorinanes was used to synthesize a phosphorylated

derivative of 1,6-dibromo-1,6-dideoxy-D-mannite. This substance is used as a medication, Myelobromol (Hungary), in the treatment of chronic myeloleukosis. The method consists of the sequential treatment of 1,2,4,3,5,6-bis-O-(phosphite)-D-mannite with bromine and a suitable nucleophilic reagent such as a secondary amine. In the present work 1,6-dibromo-1,6-dideoxy-2,4,3,5-bis-O-(N-morpholidophosphate)-D-mannite was prepared. In contrast to Myelobromol, this substance manifests an immunomodulating effect. References 7: 4 Russian, 3 Western.

UDC 547.26'118

Reaction of Thio Derivatives of Trivalent Phosphorus Acids Containing P-H Bond

18410012c Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 5 May 86) pp 1468-1473

[Article by O. G. Sinyashin, I. Yu. Gorshunov, E. S. Batyyeva, and A. N. Pudovik, Organic and Physical Chemistry Institute imeni A. Ye. Arbuzov, Kazan]

[Abstract] While primary and secondary phosphines are widely used in various branches of organic chemistry, other derivatives having amide, ester, or thioester functional groups adjacent to the P-H bond have not been well studied. These compounds are normally prepared by reduction of the corresponding trivalent phosphorus acid halide with a complex alkali metal hydride or organotin hydride. A new approach, proposed in a previous work, is based on the reaction of thioesters of these acids with trialkyltin compounds. In the present a study was made of the effect of using inhibitors and promoters on the reaction rates using organotin dihydrides. Specifically, S,S-diethylalkyldithiophosphonites and triethyltrithiophosphite were reduced with dibutyltin dihydride. It was demonstrated that the selectivity of these reactions can be controlled by using a radical initiator such as azo-bis-(isobutyronitrile) or an inhibitor such as hydroquinone. References 11: 8 Russian, 3 Western.

UDC 547.1'118

Reaction of Thiophosphoric and Thiophosphonic Acid Chlorides With Carbonyl Compounds

18410012d Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 28 Mar 86) pp 1473-1478

[Article by I. S. Nizamov, V. A. Alfonsov, E. S. Batyyeva, and A. N. Pudovik, Organic and Physical Chemistry Institute imeni A. Ye. Arbuzov, Kazan]

[Abstract] Trivalent phosphorus acid chlorides react with carbonyl compounds by splitting the P-Cl bond and forming either α -chlorophosphonic derivatives or dehydrochlorination products and condensation products of the latter. In studies involving reactions of these acid

chlorides containing a trialkyl group with α,β -unsaturated ketones, β -hydroxyketones, and aldehydes and ketones, it was demonstrated the P-S bond remains intact. Reactions of acid chlorides of thioacids having a tri-coordinated phosphorus atom with simple aldehydes and ketones in the absence of proton donors have not been studied. In the present work a study of the reactions of S-alkylthiodichlorophosphite, S,S^{prime}-diethyldithiophosphite, and S-ethylphenylthiochlorophosphite with benzaldehyde and acetone shows that these reactions, in contrast to other acid chlorides of trivalent phosphorus, take place at the P-S bond to form α -(alkylthio)alkylphosphonic derivatives, the P-Cl bond remaining intact. The reactions are accelerated in the presence of hydrogen chloride. References 13: 12 Russian, 1 Western.

UDC 547.26'118+547.391

Reaction Mechanism of Complete Esters of Phosphorous Acid With α -Unsaturated Acids

18410012e Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 11 Jun 86) pp 1478-1483

[Article by T. Kh. Gazizov, Yu. V. Chugunov, R. U. Belyalov, and A. N. Pudovik, Organic and Physical Chemistry Institute imeni A. Ye. Arbuzov, Kazan]

[Abstract] In 1956 G. Kh. Kamay and V. A. Kukhtin discovered the reaction of trialkylphosphites with α,β -unsaturated acids, which turned out to be a convenient method for the synthesis of esters of β -phosphoryl carboxylic acids. However, the mechanism of this reaction with acrylic acid has remained unclear due to insufficient data. In the present work the reaction mechanism of complete esters of trivalent phosphorus with α,β -unsaturated acids was studied in detail. The results demonstrate that diethyl(2-oxo-3-pentene-4-yl)phosphite reacts with acrylic acid at the level of its functional group to form diethylacryloylphosphite. Trivalent phosphorus esters react with acrylic and propionic acids at the carboxyl group of the unsaturated acid. References 14: 14 Russian, 1 Western.

UDC 547.341

Reactions of 2-Halogen Substituted Alkenylphosphonites With α -Halogen Carbonyl Compounds

18410012f Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 16 Apr 87) pp 1483-1489

[Article by Yu. G. Trishin, I. V. Konovalova, L. A. Burnayeva, A. F. Afanasov, I. S. Dokuchayeva, V. N. Chistokletov, and A. N. Pudovik, Paper and Pulp Industry Technological Institute, Leningrad]

[Abstract] In certain reactions 2-halogen-substituted alkenylphosphonites are capable of splitting off the halogen bound to the sp^2 -hybridized carbon atom. Realization of

this property in the case of a reaction with α -halogen carbonyl compounds could result in the preparation of phosphorus-containing heterocyclics. It has been previously demonstrated that diethyl esters of 2-bromo-1-phenylethynyl- and 2-chloro-2-ethylthioethenylphosphonic acids react with both chloral and nonsubstituted alkenylphosphonites to form alkenylphosphonates. In the present work infrared spectra showed that, in all reactions studied, 2-halogen-substituted alkenylphosphites react with α -halogen carbonyl compounds to form a straight-chain compound and that the phosphonite double bond is not directly involved in the reaction. References 6 (Russian).

UDC 547.495.1'118

Synthesis of Chlorothioformic Acid Dialkylamides and Their Reactions With Esters of Trivalent Phosphorus Acids

18410012g Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 6 Feb 87) pp 1489-1493

[Article by A. N. Pudovik, V. K. Khayrullin, and M. A. Vasyanina, Organic and Physical Chemistry Institute imeni A. Ye. Arbuzov, Kazan]

[Abstract] Both acetyl and benzoyl chlorides react with trialkyl phosphites according to the Arbuzov reaction to form esters of acetyl and benzoyl phosphonic acids. In the case of phosphites having a low nucleophilic phosphorus atom, the acyl chlorides react without affecting its coordination number to form monochloroacetates and esters of the carboxylic acid. It has been reported that the methyl ester of diphenyl phosphonous acid reacts with chlorothioformic acid dimethyl amide by the Arbuzov reaction to form diphenyl(N,N-dimethylthiocarbamoyl)phosphine oxide. In the present work the dimethyl and diethyl amides of chlorothioformic acid were prepared by the reaction of tetramethyl and tetraethylthiuramdisulfide with sulfur chloride. Both the trialkyl phosphites and the dibutyl ester of ethyl phosphonous acid react with chlorothioformic acid dialkylamides according to the Arbuzov reaction to form the dialkyl esters of N,N-dialkylthiocarbamoylphosphonic acids, respectively. Chloroformic acid dimethyl amide reacts similarly with triethyl phosphite to form diethyl N,N-dimethylcarbamoylphosphonate. References 12: 6 Russian, 6 Western.

UDC 547.421.51.262+547.26'118

Acetals Having Phosphorus Substituent at Alcohol Group

18410012g Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 23 Jan 87) pp 1493-1504

[Article by M. B. Gazizov and R. A. Khayrullin, Chemical Technology Institute imeni S. M. Kirov, Kazan]

[Abstract] The reactions of complete phosphites with aliphatic aldehydes and phosphorylated vinyl ethyl esters with alcohols are the only two methods reported thus far

for the preparation of acetals containing a phosphorus substituent at the alcohol group. However, neither method is universal, nor is either widely used owing to their low yields, the unavailability of their starting materials, and the extreme temperatures required. A new method for preparing these acetals is based on the reaction of available vinylalkyl esters with trivalent phosphorus alcohols phosphorylated in the 1-position, which are readily synthesized by the reaction of carbonyl compounds with dialkylphosphites under conditions of alkaline catalysis, or from trivalent phosphorus chlorides in a proton donor solvent. Ketoacids, activated with trialkylphosphite, react with pyrocatechinchlorophosphite mainly at the carbonyl group. Hydroxyacetals, phosphorylated at the alcohol group, react by catalytic thermocyclization to form 4-phosphorylated 1,3-dioxolanes. References 18: 17 Russian, 1 Western.

UDC 547.953+547.915

Convenient Variant of Selenone-Selenol Isomerization of Phosphorinanes. Synthesis of Selenium-Containing Analogues of Phosphohomocholines and Bis-Phosphatide Acids

18410012i Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 4 May 87) pp 1504-1512

[Article by D. A. Predvoditelev, Ye. N. Rasadkina, A. R. Bekker, and E. Ye. Nifantsev, Moscow State Pedagogical Institute imeni V. I. Lenin]

[Abstract] The present work is on the chemistry of glycerine cyclohalcophosphates. The first stage includes research on selenone-selenol isomerization of 2-seleno-2-dioxaphosphorinanes. Although this reaction has been studied very little, it has been demonstrated that cyclic systems are more difficult to convert than linear ones are. Tetraethylammonium iodide has been proposed for use as a catalyst in cyclic isomerization, and phosphonium salts have been proposed as new catalysts for thio-thiol isomerization of thio- and dithio-1,3,2-dioxaphosphorinanes, where it was demonstrated that the reaction could be used for the synthesis of original phospholipids. In the present work phosphonium salts were used for the first time as catalysts for the selenone-selenol isomerization of simple cyclic selenophosphates and for corresponding objectives in lipid chemistry. Selenium is known to play a definite role in the metabolism of proteins, fats, and carbohydrates, and for this reason selenium-containing phospholipids may be instrumental in regulating enzymatic reactions related to redox processes. Additionally, their spectral properties make them useful in membranology. Phosphonium salts were shown to induce selenone-selenol isomerization in 1,3-alkyleneselenophosphates, the substituent at the phosphorus atom having an effect on the rearrangement rate. Cyclic diacylselenophosphates react with trimethylamine to form previously unknown selenophosphohomocholines, and cyclic diacylselenophosphates also

react with potassium stearate and lithium bromide to form selenium-containing analogues of bis-phosphatidic acid. References 14: 9 Russian, 5 Western.

UDC 547.468:546.31

Double Biprotonated Oxyethylidenediphosphonates of Alkali Metals and Ammonia

18410012j Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 4 Mar 87) pp 1512-1516

[Article by Ye. G. Afonin, T. A. Matkovskaya, and N. I. Pechurova, Moscow State University imeni M. V. Lomonosov; Chemical Reagents and Ultrapure Chemical Substances All-Union Scientific Research Institute, Moscow]

[Abstract] Oxyethylidenediphosphonic acid is an important chemical reagent used to bind calcium ions into stable complexes in aqueous solutions. It also has a high chemisorption affinity for the crystals of such poorly soluble calcium salts as phosphates, oxalates, and carbonates, which makes it a way of controlling and growing these crystals in medicine and in industry. Aqueous solutions of alkali metal salts of these acids, particularly those that are disubstituted, have close-to-neutral reactions, which makes them useful in the diagnosis and treatment of calcium metabolism dysfunctions. While biprotonated sodium oxyethylidenediphosphonate has been well studied, only limited information exists on the double salts. In the present work, element and x-ray analysis, thermal analysis, and IR-spectra were used to study the compositions of NaMH_2X , where X is K, Rb, or NH_4 . Salts having the composition NaKH_2X , $\text{NaNH}_4\text{H}_2\text{X}$, and $\text{NaRbH}_2\text{X} \cdot 3\text{H}_2\text{O}$ can be crystallized from aqueous solutions. The compounds NaMH_2X (where X equals K, Rb, or NH_4) are isostructural, while the compounds $\text{Na}_2\text{H}_2\text{X}$ and NaMH_2X (where X equals K or Rb) have near-thermal resistance. Figure 1; references 11: 7 Russian, 4 Western.

Alkoxychlorophosphonyl (alkoxyfluorophosphonyl) chloromethylisocyanates

18410012k Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 13 Jan 87) pp 1516-1525

[Article by B. N. Kozhushko and V. A. Shokol, Organic Chemistry Institute, Kiev]

[Abstract] In a previous work it was demonstrated that trichloromethylisocyanate, which exists in tautomeric equilibrium with N-(dichloromethylene)carbamic acid chloride, reacts readily with diethylchlorophosphite to form a mixture of ethoxychlorophosphonyldichloromethyl- and bis(ethoxychlorophosphonyl)chloromethylisocyanates. Reaction with diethylfluorophosphite, however, resulted

only in bis(ethoxyfluorophosphonyl)chloromethylisocyanate. A study was made of the reaction of the fluorine-containing analogue of trichloromethylisocyanate, dichlorofluoromethylisocyanate, with dialkylchlorophosphites. This reaction was found to proceed according to the Arbuzov rearrangement. Dialkylchlorophosphites react with a tautomeric mixture of dichlorofluoromethylisocyanate and dichloromethylenecarbamic acid fluoride to form the title compounds. Figures 4; references 8: 6 Russian, 2 Western.

UDC 547.241

O-Alkylperfluoroalkylphosphonites

18410012l Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 28 May 87) pp 1525-1529

[Article by A. V. Golovanov, I. G. Maslennikov, and A. N. Lavrentyev, Technological Institute imeni Lensovet, Leningrad]

[Abstract] Sixteen O-alkylperfluoroalkylphosphonites were synthesized by reacting perfluoroalkyldiiodophosphines with various alcohols. The phosphorus-alkylfluoro bond is more resistant to aqueous acid solutions than to alkalis. Splitting of the alkylfluoro group from O-alkylperfluoroalkylphosphonites during alkaline hydrolysis follows second-order reaction rules and first-order rules for each component. References 8 (Russian).

UDC 541.49:546.24,131:541.67

Polar Properties of Solutions of Complexes of Tellurium Tetrachloride and Aryltellurium Chlorides With Aromatic Phosphine Oxides, Triphenylphosphine, and Triphenylphosphine Sulfide and -Selenide in Benzene

18410012n Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 25 Feb 87) pp 1561-1567

[Article by L. Ye. Rybalkina, D. Ya. Movshovich, S. B. Bulgarevich, V. A. Kogan, I. D. Sadkov, and A. A. Shvets, Rostov State University imeni M. A. Suslov]

[Abstract] The complex-forming capability of tetracoordinated tellurium derivatives have not been well studied. Interest in the molecular complexes of tellurium tetrachloride and its organic complexes revolves around the fact that the tellurium atom in tetracoordinated derivatives has both an unshared electron pair and a vacant d-orbital, which causes it to exhibit both electron donor and acceptor properties. The donor properties of a number of tetracoordinated tellurium derivatives were studied in a previous work. In the present work the acceptor properties of this type of system were studied. Dipole moments were used to study the complex formation of tellurium tetrachloride and several aryltelluriumtrichlorides with aromatic phosphine oxides, triphenylphosphine, triphenylphosphine sulfide and triphenylphosphine selenide in benzene solvent. The formation of complexes in 1:1 and 1:2 ratios as a result of donor-acceptor interaction was confirmed. The acceptor

capability of tellurium and its tetracoordinated derivatives is determined by the nature of the substituent at the tellurium atom. Figures 2; references 25: 13 Russian, 12 Western.

UDC 547.241

**Silylphosphites in Reactions With
2-o-Hydroxybenzylloxazolidines**

18410012m Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 10 Apr 87) pp 1550-1557

[Article by E. Ye. Nifantsev, T. N. Popkova, T. S. Kukhareva, and A. R. Bekker]

[Abstract] This work is a continuation of studies on polar phosphorus-containing spatially inhibited phenols with the goal of synthesizing hydroxyethylamino-o-hydroxybenzylphosphonates having varying degrees of spatial screening of the phenol hydroxyl group. To prepare these compounds, a variant of the Kabachnik-Fields reaction, based on oxazolidines, was used first since this reaction occurs under mild conditions. However, in the diethylphosphite-2-o-hydroxybenzylloxazolidine system used, a complex mixture of products was formed. This was apparently the result of intermolecular transesterification with the alcohol or phenol hydroxyl groups and alkylation. In the present work, the more nucleophilic trimethylsilylphosphites were employed, and instead of oxazolidines, the trimethylsilyl derivatives were used. It was demonstrated that oxazolidine reacts by addition at room temperature with trimethylsilyldiethylphosphite and tris- (trimethylsilyl)phosphite with close to quantitative yields to form the desired silylated hydroxyethylaminobenzylphosphonates. Hydrolysis of the latter results in the formation of acids, esters, and salts containing an aminophosphonate group in the ortho position to the phenol hydroxy group. Oxazolidines prepared from o-hydroxyacetophenols react with silylphosphites to form benzoxaphospholanes, some of which have a tertiary butyl radical in the o-phenyl position. References 6: 4 Russian, 2 Western.

UDC 547.241

**Synthesis of C-Phosphorus (III)-Substituted
Derivatives of Azomethines**

18410012q Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 7 Jul 87) pp 1663-1664

[Article by Z. S. Novikova, M. M. Kabachnik, I. A. Chabnaya, and I. F. Lutsenko, Moscow State University imeni M. V. Lomonosov]

[Abstract] It was previously demonstrated that α -C-phosphorus (III)-substituted azomethines could be prepared by reacting dichloroalkenylamidophosphites with alkylmagnesium halides, i.e. by rearranging N-phosphorus-substituted enamines into C-phosphorus-substituted

azomethines. In the present work it was demonstrated that lithium derivatives of azomethines react readily with dialkylchlorophosphines to form C-phosphorus (III)-substituted derivatives of azomethines with 73-85 percent yields. References 2: 1 Russian, 1 Western.

UDC 547.241

**Reactions of Lactam Alkylation Products With
Sodium Salts of Dialkylphosphites**

18410012r Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 8 Jul 87) pp 1668-1669

[Article by V. Yu. Mavrin, V. V. Moskva, and T. N. Apalkova, Chemical Technical Institute imeni S. M. Kirov, Kazan]

[Abstract] It has been found previously that the direction of the reaction of carbonium salts, prepared by alkylation of N-substituted lactams, with sodium salts of dialkylphosphites depends not only on the size of the heterocycle and the nature of the carbonium salt anion but also on the order in which the reagents are combined. In the present work the sodium salt of diethylphosphorous acid was found to react with O-methyl-N-methylpyrrolidonium, -methylpiperidonium, and -azepinonium methylsulfates, as well as with O-ethyl-N-methylpiperidonium tetrafluoroborate to yield the corresponding phosphonates. References 2: 1 Russian, 1 Western.

UDC 547.241

**Condensation of Diethylphosphite With Mixed
Derivatives of Orthocarbonic Acid**

18410012s Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 8 Jun 87) p 1670

[Article by V. V. Moskva and V. Yu. Mavrin, Chemical Technological Institute imeni S. M. Kirov, Kazan]

[Abstract] Condensation of diethylphosphite with orthocarbonic acid esters results in the formation of the diethyl ester of triethoxymethylphosphonic acid. In the present work it has been observed that mixed esteramides of orthocarbonic acid, N,N,N,N-tetramethyldiaminodithoxymethane and N,N-dimethylaminotriethoxymethane, react with diethylphosphite (in a 1:2 ratio of the reagents) to form one and the same products,

diethyl ester of N,N-dimethylaminoethoxymethylphosphonic acid and triethylphosphate. Changing the ratio of reagents has no effect on the direction of the reaction. References 3 (Russian).

UDC 547.79+547.468

**Reaction of
N-(Triphenylphosphoniomethyl)benzimidoyl
Chloride Carboxylic Acid Chlorides**
18410012t Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 7, Jul 88 (manuscript
received 6 Jul 87) pp 1670-1671

[Article by O. B. Smolii, V. S. Brovarets, and B. S. Drach, Bioorganic Chemistry Institute, Kiev]

[Abstract] It has been observed that phosphorus-containing imidoyl chloride, despite being a pronounced electrophilic reagent, reacts readily with various other nucleophilic reagents as well as with certain electrophiles. The condensation of this compound with aromatic carboxylic acid chlorides is presented as an example. Intermediate compounds are formed during the course of the reaction that, in the presence of triethylamine, are capable of intramolecular heterocyclization. The structures of the intermediate salts were confirmed. References 2 (Russian).

UDC 541.11.123

**Phase Equilibria in β , β' -Oxidipropionitrile-
Ethylene Glycol-Decanol, Dodecanol Systems**
18410036a Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript
received 13 Apr 87) pp 1723-1729

[Article by I. K. Zhuravleva and I. M. Basharova, Bashkirian State University imeni the 40th Anniversary of October, Ufa]

[Abstract] Experimental results are presented from an investigation of phase transformations in systems in which all the boundary systems have limited solubility of the components in the liquid state with an upper critical dissolution temperature. Phase states were studied by a visual polythermic method. The development of three-phase equilibria was traced by studying phase changes from the critical temperatures to the nonvariant monotectic temperature in three-phase systems. A critical node was found in the two-phase area, from which the three-phase equilibrium develops. The temperature at which the solid phase appears was studied in decanol isoconcentrates. Three-phase liquid equilibrium appears only in systems with nonanol, decanol, and undecanol. A three-phase liquid equilibrium was found in the system nitrile-glycol-decanol at 16.5°C, developing from the

critical connode at temperatures below the critical temperatures of all three boundary separations and ending in the crystallization field of the alcohol. Figures 4, references 4: 3 Russian, 1 Western.

UDC 547.1'118

**Acetylthiophosphites. Synthesis, Isomerism, and
Certain Transformations**
18410036b Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8, Aug 88 (manuscript
received 8 Sep 86) pp 1734-1740

[Article by V. A. Alfonsov, D. A. Pudovik, R. A. Musin, V. N. Nazmutdinova, Yu. Ya. Yefremov, E. S. Batyeva, and A. N. Pudovik, Institute of Organic and Physical Chemistry imeni A. Ye. Arbusov, Kazan Branch, USSR Academy of Sciences]

[Abstract] Continuing a study of mixed organic acid and thioacid anhydrides of trivalent phosphorus, the authors studied acyl derivatives of the dialkylthiophosphorus acids. Phosphorylation of thioacetic acid and its derivative trivalent phosphorus compounds primarily formed S-phosphorylation products, acetylthiophosphites. O-phosphorylation is a minor result of the reaction. The O- and S-isomers regroup in the presence of methyl iodide and form acetyl phosphonates. The reactions of acetylthiophosphites with proton-containing nucleophilic reagents occur at the phosphorus atom and yield acetylthio group substitution products. References 10: 8 Russian, 2 Western.

UDC 547.1'118

**Interaction of (Acetylthio)phosphites With
Hydrogen Chloride, Acid Chlorides, and Chloral**
18410036C Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript
received 17 Nov 86) pp 1740-1744

[Article by V. A. Alfonsov, D. A. Pudovik, E. S. Batyeva, and A. N. Pudovik, Institute of Organic and Physical Chemistry imeni A. Ye. Arbusov, Kazan Branch, USSR Academy of Sciences]

[Abstract] A study examined the reactivity of dialkyl (acetylthio)phosphites with hydrogen chloride, P^{III} acid and carboxylic acid chlorides, and chloral. In contrast to alkylthio derivatives, the (acetylthio)phosphites were found to react with dry hydrogen chloride at room temperature in an Arbuzov reaction involving acetylthio groups and yielding dialkylthiophosphites and acetyl chloride. Substitution of the acetylthio group was also frequent. Replacement of the alkyl group with an acetyl group at the sulfur atom of P^{III} acid thioderivatives increases their activity in attachment reactions. Ethylphenylchlorophosphine enters an acetylthio group and

chlorine exchange reaction at the P^{III} atoms. Attachment products are formed in the reaction with chloral. References 14: 10 Russian, 4 Western.

UDC 535.338:541.63

Oscillation Spectra and Structure of Tris-(Dialkylidithiophosphate) Phosphites
18410036d Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript received 6 Apr 87) pp 1744-1752

[Article by S. A. Katsyuba, Ye. A. Filippova, V. A. Alfonsov, R. R. Shagidullin, V. N. Shegeda, and D. A. Pudovik, Institute of Organic and Physical Chemistry imeni A. Ye. Arbusov, Kazan Branch, USSR Academy of Sciences]

[Abstract] A study examined the IR and Raman spectra of $[(CH_3O)_2P(S)S]_3P$ (I) and $[(C_2H_5O)_2P(S)S]_3P$ (II), in order to discover information on the possible existence and structure of molecular coordination bonds $P^{III}-S=$. The force fields of (I) and $(CH_3O)_2P(S)SH$ (III) are compared, eliminating the influence of kinematic factors and noncharacteristic oscillations. The hypothesis of the formation of coordination phosphorus-sulfur bonds is not confirmed by the oscillation spectra. Molecular mechanics calculations indicate that the reason for the observed shortening of distance between the thion sulfur and P^{III} atoms in comparison with the sum of their Van der Waals radii is forced packing of the atoms in the molecule as a result of steric and electrostatic intramolecular interactions. Internal rotation occurs within the phosphite atoms around the PO and probably also PS bonds. Figures 3, references 13: 12 Russian, 1 Western.

UDC 547.61'541.6

Photoelectric Spectra and Electron Structure of Organophosphorus Compounds. VII. Nonempirical Calculations
18410036e Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript received 9 Dec 86) pp 1752-1758

[Article by V. V. Zverev and R. G. Islamov, Institute of Organic and Physical Chemistry imeni A. Ye. Arbusov, Kazan Affiliate, USSR Academy of Sciences]

[Abstract] Continuing their analysis of the electron structure, ionization potentials, and composition of several organophosphorus compounds, the authors compare the results of nonempirical computations with each other and with experimental values of ionization potential. Phosphorus-containing compounds with the vinyl group were computed in the cis-form with bond lengths considered constant. The computations are used to establish the relationship of orbital energies with the experimental values of potentials. This yields information on the

distribution of electron density, the structure of the phosphoryl and double bonds, and the energy and composition of the valent and internal orbitals. References 12: 8 Russian, 4 Western.

UDC 547.26'118

Synthesis and Certain Reactions of O, O-Diaryldithiophosphoric Acids and Their Derivatives
18410036f Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript received 9 Feb 87) pp 1778-1784

[Article by B. A. Khaskin, N. A. Torgasheva, and O. D. Sheluchenko, All-Union Scientific Research Institute of Chemical Plant Protectants, Moscow]

[Abstract] The authors synthesized disulfides (I) containing chlorophenoxyl groups at the phosphorus atom as substituents and studied their chemical properties. It was found that reacting phosphorus pentasulfide with mono-, di-, and trichloro-substituted phenols in boiling xylene provided a good yield of the corresponding dithiophosphoric acids (II). Interaction of acids (II) with amines and ammonia in ether or benzene at less than 20°C yielded ammonium salts (III). Reaction of bis[di(aryl)thiophosphoro] and bis[di(aryloxy)thiophosphoro] disulfides with diazomethane causes the insertion of a methylene group at the S-S bond of the disulfide molecule. References 4: Russian.

UDC 547.468.1'466.22

Acid Dissociation of 3-Phosphonomethylene Sydnone
18410036g Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript received 17 Apr 87) pp 1857-1860

[Article by F. F. Khizbullin and B. P. Strunin, All-Union Herbicides and Plant Growth Regulators Scientific Research and Technological Institute, Ufa]

[Abstract] This article presents a study of the structure and acid-base properties of 3-phosphonomethylene sydnone (3-PMS). The variation of chemical shifts in the labeled ^{31}P and ^{13}C nuclei in aqueous solutions of 3-PMS were studied as functions of pH between 1.4 and 13. Spectral studies indicated no measurable change in the chemical shifts of the two labeled atoms upon dissociation of the most acid proton since the substrate was found to be unstable in strongly acid media. The acid dissociation constants of 3-PMS were determined in

water. Throughout the measured pH range, the compound does not form a betaine structure. Figure 1, references 10: 2 Russian, 8 Western.

UDC 547.496.1'118.5

Synthesis of N-Alkyl(Aryl)-N-(Diethylphosphoryl) Sulfinylcarbamates

18410036h Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript
received 6 Jul 87) pp 1915-1916

[Article by Yu. Yu. Klyatskiy, V. A. Kolesova, and Yu. A. Strepikheyev, Moscow Chemical Technology Institute imeni D. I. Mendeleyev]

[Abstract] A study examined the reaction of N-chlorosulfinyl carbamates with triethylphosphite, and it is shown that the reaction is an Arbuzov reaction. The reaction was performed under various conditions in benzene, ether, THF, and without solvent with cooling to 0°C. The reaction of N-alkyl- and N-arylchlorosulfinyl carbamates with triethylphosphite yields N-methyl-(I) and N-phenyl-N-(diethylphosphoryl)sulfinyl carbamate (II). Its IR and PMR spectra are described. References 3: 2 Russian, 1 Western.

UDC 547.26'118

Thermal Isomerization of Methyltrichloromethyl Phosphonite

18410036l Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript
received 11 May 87) pp 1916-1917

[Article by T. Kh. Gazizob, L. N. Usmanova, and A. N. Pudovik, Institute of Organic and Physical Chemistry imeni A. Ye. Arbusov, Kazan Branch, USSR Academy of Sciences]

[Abstract] The authors found that methyltrichloromethyl phosphonite (I) isomerizes to form a self-alkylation product—methyltrichloromethyl phosphinic acid. The reaction is completed in a sealed ampule in 3 hours at 120°C and in 1 hour at 145°C. It was found that (I) interacts with HCl at 80°C to form trichloromethylphosphite. When triethylamine is added to (I), an exothermic reaction occurs, and dimethyltrichloromethylphosphonite is formed. The proposed reaction mechanism is diagramed. References 2: 1 Russian, 1 Western.

UDC 547.341

Dihalogenocyclopropylmethylphosphonites

18410036j Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript
received 15 Jul 87) pp 1918-1919

[Article by B. G. Liorber, G. V. Urmancheyeva, V. A. Pavlov, and T. I. Yevdokimova, Kazan Institute of Chemical Technology imeni S. M. Kirov]

[Abstract] The authors discovered that dichloro(bromo)cyclopropylmethylphosphonates can be obtained by attaching dichloro(bromo)carbenes to allylphosphonates

by using mixed-phase catalysis. The electronegative phosphorus-containing substituent present in the olefin molecules hinders attachment, which requires that the reaction conditions be somewhat modified: an olefin:haloform:50 percent aqueous NaOH solution ratio of 1:10:14 for dichlorocyclopropylmethylphosphonates; the catalyst triethylbenzyl ammonium chloride in the amount of 6 molecular percent relative to the alkene; a ratio and molecular percent content of 1:5:5 and 10 percent, respectively, for dibromocyclopropylmethylphosphonate; and a heating time of 4 hours at 60°C with intensive agitation. Dichlorocyclopropylmethylphosphonates were produced with a 45-66 percent yield, and dibromocyclopropylmethylphosphonate was produced with a 30 percent yield per allylphosphonate. The structures were verified by NMR and IR spectroscopy plus elemental analysis. References 4: 2 Russian, 2 Western.

UDC 547.26'118

Meta(β -dialkoxylphosphorylvinyl) Monobenzo-15-Crown-5

18410036k Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript
received 3 Jul 87) pp 1920-1921

[Article by V. I. Kalchenko, N. A. Parkhomenko, L. I. Atamas, and L. N. Markovskiy, Institute of Organic Chemistry, Ukrainian Academy of Sciences, Kiev]

[Abstract] A method is suggested for the phosphorylation of crown ethers that does not require transformations of the phosphorus atom and that allows synthesis of crown ethers that are functionalized by a variety of phosphorus-containing groups, including chiral groups. The method is demonstrated by the palladium-catalyzed vinylation of m-bromo-monobenzo-15-crown-5 with vinylphosphonates in a reaction that occurs stereoselectively, forming m-(β -dialkoxylphosphorylvinyl) monobenzo-15-crown-5 with a trans configuration of the multiple bond. References 5: 2 Russian, 3 Western.

UDC 547.341

Interaction of Trialkylphosphites With 1,1-Diacyl-3,3,3-Trichloropropenes

18410036l Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript
received 19 Jun 87) pp 1921-1923

[Article by D. M. Malenko, N. V. Simurova, and A. D. Sinitsa, Institute of Organic Chemistry, Ukrainian Academy of Sciences, Kiev]

[Abstract] The reaction of 1,1-diacyl-3,3,3-trichloropropenes with trialkylphosphites leads to unsaturated phosphonates that, depending on the structure of the acyl groups, are present in enol or ketone form. The change in direction of phosphorylation with the

trichloroethylidene derivatives of β -dicarbonyl compounds is apparently connected to the presence of three electron-acceptor substituents at the ethylene bond, which increases the electrophilicity of the C^2 propene chain, which is apparently the site of the phosphorus atom attack. The structure of the phosphonates produced is confirmed by PMR, NMR, and IR spectroscopy. References 2: 1 Russian, 1 Western.

UDC 547.241

Dechlorination of Spatially Hindered Amidotrichloromethylphosphinous Acid Chlorides
18410036m Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript received 1 Apr 87) pp 1923-1925

[Article by A. P. Marchenko, G. N. Koydan, V. A. Oleynik, and A. M. Pinchuk, Institute of Organic Chemistry, Ukrainian Academy of Sciences, Kiev]

[Abstract] It is suggested that amidotrichloromethylchlorophosphonates will react with tertiary phosphines in accordance with a halogenophilic mechanism, with the carbanion initially formed stabilized by β -elimination of the chlorine atom from the phosphorus, forming λ^3 phosphaethylenes, like the reaction of phosphines with hexachloroethane. The authors have confirmed this by way of the examples of spatially hindered dialkylamidotrichloromethylchlorophosphonites obtained by nucleophilic trichloromethylation. References 6: 4 Russian, 2 Western.

UDC 547.26'118

Bicyclic Phosphorus-Containing Polyesters
18410036n Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript received 1 Apr 87) pp 1925-1926

[Article by A. A. Chaykovskaya, T. N. Kudrya, R. I. Yurchenko, O. M. Voytsekhovskaya, and A. M. Pinchuk, Institute of Organic Chemistry, Ukrainian Academy of Sciences, Kiev]

[Abstract] Continuing their studies of the coordination properties of macrocyclic polyesters containing a four-coordinated phosphorus atom in the ring, the authors synthesized macrocycles with bicyclic structure. Adamantane-1,3-di[phosphonyl(dibenzo-14-crown-5)] and adamantane-1,3-di[phosphonyl(dibenzo-17-crown-6)] were synthesized by reacting adamantane-1,3-diphosphonic acid tetrachloride with the disodium derivatives of diphenyls in very dilute solutions. A study of the complex-forming properties of the macrobicycles synthesized by a modified solubility method in a number of

alkali and alkali-earth metal picrates showed that these compounds are effective complexing agents for the cations studied. References 7: Russian.

UDC 547.241

Interaction of Phosphorylated Orthoformates and Formals With Diethylchlorophosphite
18410036o Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript received 16 Jul 87) pp 1927-1928

[Article by A. A. Prishchenko, M. V. Livantsov, N. V. Boganova, and I. F. Lutsenko, Moscow State University imeni M.V. Lomonosov]

[Abstract] Trialkyl orthoformates react smoothly with dialkyl chlorophosphites to form phosphorus (V)-substituted formals. The reaction of phosphorylated trialkyl orthoformates with diethyl chlorophosphite proceeds differently, the reaction being directed toward the phosphoryl group of the trialkyl orthoformates and leading to products of the splitting of the phosphorus-carbon bond: tetraethylpyrophosphite and diphosphane monoxide. The reaction scheme suggested includes the initial electrophilic attachment of diethyl chlorophosphite at the phosphoryl group, which means that the breaking of the phosphorus-carbon bond occurs in an intermediate quasiphosphonium adduct. References 4: 3 Russian, 1 Western.

UDC 547.241

Attachment of Acylphosphonites at Carbonyl Group

18410036p Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 8 Aug 88 (manuscript received 16 Jul 87) pp 1928-1929

[Article by A. A. Prishchenko, M. V. Divantsov, N. V. Boganova, and I. F. Lutsenko, Moscow State University imeni M. V. Lomonosov]

[Abstract] The reaction of acylphosphonites with aromatic aldehydes and α -ketophosphonates is found to occur with the breaking of the phosphorus-carbon bond and the formation of attachment products at the carbonyl group, i.e., substituted phosphites. The reaction apparently begins with an attack by the electrophilic 3-coordinated phosphorus atom on the oxygen atom of the carbonyl group and the formation of a bipolar adduct, the stabilization of which is accompanied by the breaking of the phosphorus-carbon bond and the migration of the acylium cation to the central carbon atom. The rate of the attachment reaction is determined by the reactivity of the carbonyl group, which is related to the spatial and electronic effects of the substituents in the initial aldehydes and α -ketophosphonates. The reaction occurs easily with boiling of a mixture of aldehyde and acylphosphonite in methylene chloride or brief heating of a mixture of acylphosphonite and α -ketophosphonate at 50-90°C. The characteristic yellowish green color of the initial acylphosphonites disappears when the reaction is completed. References 3: Russian.

UDC 547.39+581.1

**Synthesis and Herbicidal Activity of
4-Chloro-2-nitroanilides of Aromatic and
Heterocyclic Acids**

18410011e Tashkent UZBEKSKIY KHIMICHESKIY
ZHURNAL in Russian No 3, May-Jun 88 (manuscript
received 28 Dec 87) pp 61-62

[Article by M. A. Khaydarov, A. A. Umarov, Sh. Israi-
lova, L. V. Molchanov, and A. T. Ayupova, Plant Chem-
istry Institute, UzSSR Academy of Sciences]

[Abstract] N-acylation of aromatic amines is used in the
synthesis of pesticides. In the present work 11 new
herbicides were prepared by acylation of 4-chloro-2-
nitroaniline with various aromatic and heterocyclic
acids in the presence of phosphorus pentoxide. Struc-
tures of the compounds were confirmed with IR-spectra,
and tests run on various vegetables showed that phenox-
ybutyric acid 4-chloro-2- nitroanilide is the most active.

The herbicidal activity of the anilides is a function of the
structure of the side chain and the nature of the substit-
uent in the benzene ring. References 3 (Russian).

UDC 632.954:633.63:631.587

**Estimate of Influence of Mixtures of
Postsprouting Herbicides in Sugar Beet Fields
With Irrigation**

18410039e Moscow AGROKHIMIYA in Russian
No 8, Aug 88 (manuscript received 1 Apr 87) pp 94-98

[Article by I. M. Nikulnikov, All-Russian Sugar Beets
and Sugar Scientific Research Institute, Ramon, Voron-
ezhsk oblast]

[Abstract] Weed control studies were performed in an
irrigated experimental field consisting of thick moderately
alkaline chernozem containing 5.0-5.2 percent humus in the
top 30 cm layer. Herbicides were applied twice, and weed
thickness was rated before each application, after the appli-
cation, and at the end of the vegetation period. Mixtures of
betanal and carbodimedon were effective against young,
predominantly grassy weeds, while betanal alone was effec-
tive against predominantly dicotyledonous weeds. Betanal
plus lontrel was effective against mixed weeds. Betanal,
carbodimedon, and lontrel achieved maximum effective-
ness while slightly reducing the sugar beet harvest. None of
the herbicides had a negative influence on the crop. Refer-
ences 5: Russian.

Poor Resource Management in Oil Industry Described

18410069b Moscow SOTSIALISTICHESKAYA
INDUSTRIYA in Russian 16 Oct 88 p 1

[Article by Vladislav Krukovskiy: "What Crash Campaigns Cost Us"; first paragraph is SOTSIALISTICHESKAYA INDUSTRIYA introduction]

[Text] We are never at a loss for people in the economy who want to be in charge. And life offers us numerous examples of how costly this is to us. Of course, in this area we could and should appeal to the personal qualities of people, and executives first of all: Resist more boldly, be steadfast. Nonetheless, it was a wise man who said that people should demand from benefactors in accordance with their capabilities, and not in accordance with our wishes. This is precisely why the Law on Enterprises became necessary, to harness the energy of those who like to give orders whether they are needed or not, and remain unanswerable for their consequences at that.

A tilt toward lower oil production has revealed itself in recent years among oilmen of the Komi republic. The causes of this are complex. The geological prospectors ground to a halt, being unable to discover a single major deposit near existing oil fields in either the last or the present five-year plan. And the extractors had their share of problems as well. It was in this situation that news of an oil gusher in the Bagan area arrived. This was just half a hundred kilometers from Usinsk.

The oilmen received the news with tremendous interest, and they began waiting for the results of detailed prospecting with hope and impatience. But the party oblast committee saw things differently—it was in a mood to give orders. "Lay the pipes to Bagan!"—such was the categorical slogan that was born at this late hour. Naturally the pipeline was not in the plans of the builders and the oilmen. Moreover, many specialists voiced their doubts: Laying pipes of substantial diameter for who-knows-what is foolhardy.

But persistent pressure upon executives, and the habit they developed over the years of saluting anything that moves, had its effect. A pipeline 42 kilometers long was planned and laid at a shock pace by the collective of Glavkomigazneftstroy. Experimental derricks arose on the barren tundra as if from beneath the ground. The geologists obediently came up with a substantial figure for the deposit's reserves.

Two years went by, and now what? Fuel is barely flowing through the railroad pipeline. Prospecting carried out in parallel with the construction revealed that with great difficulty, some quantity of oil could be scraped together from this deposit, but it was scattered over a rather sizable area.

"We spent over 5 million rubles to lay pipe to the area and to organize extraction," said N. Gadzhiyev, Kombineft Association deputy general director for economics. "We cannot expect any return from this investment in the foreseeable future."

"And if this sizable amount of money had been invested by the oilmen into developing the old deposits, could there have been a real gain in oil?"

"Without a doubt," replied Nabi Saidovich, "we could have used it far more sensibly. And besides, the oilmen also have an abundance of social problems that need to be solved."

But that was before, some might say, and things are changing. No, they're not. Little is changing in the way the oil extraction sector is being managed. Thinking economically is making headway slowly, excruciatingly slowly. The oilmen have barely started to work in this direction. The special importance of the sector and its great role in the country's economy still remain a firm excuse for holding the collectives on a tight rein. Moreover as before, their executives remain between a rock and a hard place—the oblast committee on one side and the ministry on the other.

Let me tell you about one crash campaign that was organized in this instance by orders from the USSR Ministry of Petroleum Industry under the cover of talk about the rights of collectives.

The republic's oilmen drew up a detailed program for increasing production in order that extraction in the European North could be reduced by 1990. A very complex, unique deposit—Kharyagi—is being actively developed for this purpose. The oilmen have leaped further as well, toward the Arctic Ocean, to the Khylichuyu deposit. The oil there is also hard to get, but at least the reserves were confirmed long ago, and the prospects are clear. A power transmission line, a road and a pipeline to the deposit were planned with a full commitment of effort. Even some of the basic support work was started—laying the road bed and creating the necessary support base. Many times I talked on this subject with the association's former general director, Anatoliy Stepanovich Gumenyuk.

The work was continued by his successor Yu. Baydikov, albeit more slowly. Then suddenly the flywheel, which had gathered momentum by now, was stopped dead in its tracks. There is nothing bad of course in selecting a new direction. If it were a better one. But it is no less important for the oilmen themselves, who are working in self-financing conditions, to believe that this was the right thing to do. But no, the new path was charted and approved for the northerners in Moscow, on Moris Torez Street. What was selected in the opinion of capital-based executives was a better road to "big oil." It stretched across all of the Bolshezemelskaya tundra to

the Olenyaya area, where Arkhangelskgeologiya Association prospectors sank one well producing a good flow of fuel. USSR First Deputy Minister of Geology F. Sal'manov, who visited here soon after this, drew such a captivating picture of this discovery that Arkhangelsk Oblast executives immediately hastened to name the new deposit after the 70th anniversary of the Great October Socialist Revolution.

The scope of the following crash campaign was truly astounding. All efforts to plan the development of the Khylichuyu deposit were abandoned. The prospectors quickly roughed out the route of a road and a power line to the new area, and trains of tractor-drawn sleds carrying equipment and housing units made their way there on winter roads. Last winter they had planned to carry in a hundred thousand tons of cargo, but thank God, they were able to ferry in only a fourth of what they planned, including around a dozen drilling rigs. The Ministry of Petroleum Industry declared development of the new jubilee deposit to be the principal direction of work of the republic's oilmen for the next few years.

One would think that an effort of such scope, and such fast and competent concentration of resources, would bring joy to the heart. But specialists of the association and of the PechorNIPIneft institute anxiously kept going over and over the plans and the stratigraphic sections of the area, shrugging their shoulders. No one could understand why the ministry initiated this crash campaign so enthusiastically. Nonetheless, no one spoke out. Developed over the years, the principle of minding your own business was upheld in this instance as well.

But not everyone remained silent. The following dialogue occurred between A. Tsekhmeistryuk, the deputy director of PechorNIPIneft, and G. Turchaninov, chief of this institute's geological department.

Tsekhmeistryuk: Gennadiy Nikolayevich, we need to draw up plans for trial exploitation of the Deposit imeni 70-Letiye Oktyabrya on priority. Those are the ministry's orders.

Turchaninov: Whatever you say, but I'm not going to draw up any such plan.

Tsekhmeistryuk: Why? What's wrong?

Turchaninov: Because they're backing nothing but water wells. No one has found any oil up there yet.

Tsekhmeistryuk: Well, all right then, someone else will draw up the plans.

As I remember, I was also interested in this highly unexpected turn of events. One day on a visit to Arkhangelsk I decided to interview Arkhangelskgeologiya Association's chief geologist, B. Yaralov. I wanted to find out

precisely what it was that caused the oil extracting sector to point the prospectors in a new direction. Boris Afanasyevich's reply was perplexing in the least:

"We discovered good deposits of oil long ago on both sides of this area, on the east and on the west," he said. "The question then is, why shouldn't there be good deposits between them?"

But nature did not reckon with such simple logic. Moreover, is it really wise to base the future of an entire sector on such flimsy predictions? Nonetheless, the document that Turchaninov refused to have anything to do with was drawn up anyway. Around 15 million rubles were spent on importing cargo and equipment. They weren't able to get any farther. Thanks to the prospectors for that. They tested one exploratory well in the new area after another. Most of them came up dry. Now we need to pull all of the rigs, equipment and housing units for oilmen back out of the pretentiously named deposit. This job will actually cost even more. First Deputy Minister of Petroleum Industry V. Filanovskiy, who visited here recently, made the sole valid decision: to mothball part of the equipment delivered to the Olenyaya area and transfer some of it to the geologists.

Such are the woeful consequences of the desire to be in charge of everyone and everything. Such persons have been condemned in every way possible in the press and in official party documents, but nothing ever comes of it. And what we are dealing with is not just simply the waste of almost 70 million rubles, though such amounts are not small even at the scale of the entire country: There is also the loss of time! There is good reason why it is sometimes said to be more valuable than money. And finally, what do we do now to encourage the people to finish what they had abandoned previously, how do we persuade them that success depends on them, and only on them?

Nor can we be blind to the root causes of these multi-million expenditures, which have brought confusion into the organization of an important effort. These causes stretch like a comet's tail out of yesterday. There is the bureaucratic, dictatorial style of leadership in the sector. There are grounds for saying that some workers of the Komi Oblast party committee are guilty of such a style as well. It is no accident that Second Secretary Yu. Spiridonov was subjected to serious criticism for this at a recent plenum.

There is one other thing I would like to talk about—obedience. We have always raised it on a pedestal as something good. Obedience is better than fasting and prayer, so the old saying goes. Proponents of the dictatorial style of management place special value on it. Carrying out orders is still the yardstick by which the quality of a worker is measured, and the criterion of his responsibility, rather than coming up with one's own ideas and seeing them through. We know quite well today the kind of brier patch such thinking gets us into. It seems as if the bitter lessons have also made the

oilmen realize that blind obedience is a dead end. A. Fedorov, secretary of the Komineft Association's party bureau, summed up the situation in this way:

"We yielded to adventurism, and did not stand up to pressure."

He was right.

UDC 665.63/338(075.8)

Comparative Efficiency of Truck Operation on Liquid and Gas Motor Fuels

18410041a Kiev *KHIMICHESKAYA*

TEKHOLOGIYA in Russian No 5, Sep-Oct 88

(manuscript received 15 Oct 87) pp 3-8

[Article by V. A. Bugrov, G. S. Lutsker, G. G. Matusevich, and N. I. Kozlovskiy, Physical Organic Chemistry and Coal Chemistry Institute, Donetsk]

[Abstract] About 100 million rubles are spent annually in Moldavia for the delivery of oil products. In the Ukraine, about 80 percent of all freight is transported by truck, which consumes about 32 percent of the total gasoline and diesel fuel requirements. The rapid pace at which truck transport is being developed is expected to continue into the future, and the increased growth in demand for motor fuel will outstrip the supply, making it urgent to find alternate solutions to the fuel supply problem such as more rational utilization of oil products and more extensive refining. By the end of the 12th Five-Year-Plan, oil refining in the USSR is expected to reach 65 percent. This should be differentiated according to economic region with respect to present and expected fuel-energy balances and economic conditions in each region. Another solution is to use alternate motor fuels, which is made possible through the increased growth in natural gas production. The network of compressed gas dispensing stations is expected to increase so as to be able to handle 10 percent of the total truck transport needs. Estimates (for the period from 1986 to 1990) of the comparative efficiency of using gasoline derived from more extensive oil refining in the UkSSR versus the use of natural gas compressed to 20 MPa indicate that liquid fuel is more effective. References 3 (Russian).

UDC 621.431.721.75.004.14:351.777

Comparison of Ecological Characteristics of Diesel and Gas-Diesel Engines

18410041b Kiev *KHIMICHESKAYA*

TEKHOLOGIYA in Russian No 5, Sep-Oct 88

(manuscript received 8 Dec 87) pp 8-13

[Article by N. A. Gurevich, V. L. Aksenov, and V. P. Kuts, Gas Institute, Kiev]

[Abstract] In 1986 urgent measures to increase the use of natural gas as a motor fuel were adopted by the government. However, the ecological consequences of this

program must still be evaluated. In the present work results are presented on a study of the emissions from a YaMZ-240 diesel engine operating on straight diesel fuel as compared with gas-diesel operation using a natural gas-air mixture in the intake and 18-24 percent liquid diesel fuel for ignition. The results indicate that nitrogen oxides are the main contributors to the toxicity in gas-diesel operation whereas carbon is the main contributor in straight diesel operation. A universal approach to the ecological evaluation of truck exhausts is proposed. Figure 1; references 11: 10 Russian, 1 Western.

UDC 621.436

Development and Study of Fuel Supply and Control System for YaMZ-240GD Gas-Diesel Engine

18410041c Kiev *KHIMICHESKAYA TEKHOLOGIYA*

in Russian No 5, Sep-Oct 88 (manuscript received

22 Sep 87) pp 13-15

[Article by K. Ye. Dolganov, V. S. Verbovskiy, G. V. Kulich, and S. B. Kubenko, Gas Institute, Kiev]

[Abstract] The use of natural gas as a motor fuel is expected to extend fuel resources and lower air pollution as well. Conversion to gas fuel becomes even more significant in view of the expected increased output of heavy-load open-pit dump trucks earmarked for production during the 12th Five-Year-Plan. In converting these trucks to compressed natural gas, it is very important to be able to switch back and forth from liquid diesel to gas, even while the vehicle is moving. The Kiev Truck Highway Institute and the Gas Institute developed a fuel supply and control system for a BelAZ dump truck being refitted from a YaMZ-240 diesel to a YaMZ-240GD gas-diesel engine. Test results on the new system show a 4-5 percent increase in maximum power, a 70-80 percent savings in diesel fuel, and a drop in harmful exhaust emissions. Figures 3.

UDC 62-621.2.51.001.57

Mathematical Modeling of Engineering Plan for Truck Compressed Gas Filling Station

18410041d Kiev *KHIMICHESKAYA*

TEKHOLOGIYA in Russian No 5, Sep-Oct 88

(manuscript received 20 Feb 88) pp 16-21

[Article by T. Ye. Kanevets and M. R. Petrik, Compressor Machine Building All-Union Scientific Research Institute]

[Abstract] Mathematical modeling on a computer appears to be the best means for optimizing an engineering plan for a truck compressed gas filling station that includes the station's components and operating modes. The present work presents a complex mathematical model of a truck compressed gas filling station. The model, which has been developed from a systems analysis standpoint, is geared toward design optimization for

the serial production of such stations. The plan includes piston compressors for filling truck gas bottles, heat exchangers for stepped cooling, separators and gas filters, drying and regeneration systems, gas storage tanks, and ancillary equipment. Figures 4; references 3 (Russian).

UDC 662.279.8.05:665.662

**Method for Treating Natural Gas-Containing
Congealable Paraffins in Condensate**

18410041e Kiev *KHIMICHESKAYA
TEKHNOLOGIYA* in Russian No 5, Sep-Oct 88
(manuscript received 3 Feb 88) pp 22- 26

[Article by A. P. Klimenko, Ye. I. Naumov, R. F. Lavrentovich, and N. A. Kochergin, Kiev Branch, VNI-IPKtekhorgneftegazstroy]

[Abstract] Natural gas condensates from certain deposits in the USSR contain high-pour point hydrocarbons, while some from Turkmenia contain solid paraffins. This necessitates providing some means for dealing with the paraffin deposits in gas transfer and handling facilities. These deposits are normally removed by heating and passing a piston through the pipeline or by feeding reagents such as solvents or surfactants into the pipeline at the well head. However, neither method completely removes all deposits. The present work proposes a new method that consists of converting the higher gas condensate hydrocarbons into methane and carbon dioxide with steam in the presence of a nickel catalyst. A flow diagram and optimum conditions for the experimental unit used at the Sovetabads gas condensate deposit (TuSSSR) are presented. Experiments show that C_{16} - C_{32} paraffin hydrocarbons can be converted to methane. The method may be used at deposits containing 6-32 g/m³ congealable paraffins. References 15 (Russian).

UDC661.96:658.011.46

**Decreasing Energy Consumption in Chemical
Industry**

18410131b Kiev *KHIMICHESKAYA
TEKHNOLOGIYA* in Russian No 1, Jan-Feb 89
(manuscript received 19 Apr 88) pp 27-37

[Article by L. A. Kadygrob, Physical Organic Chemistry and Coal Chemistry Institute, Donetsk]

[Abstract] Ammonia and methanol are the major high volume products of the chemical industry. Construction of large scale ammonia complexes and putting them on stream remains a basic task in the USSR. During the 11th Five Year Plan ammonia production increased 5,600,000 tons per year reaching a total of 22,900,000 tons per year. Most of the ammonia was produced in aggregates having a capacity of 450,000 tons per year. According to data from the Sabic firm, methanol demand in the capitalist countries will increase eight percent annually and by 1990 methanol production will reach 25,000,000 tons annually. Consumption of methanol as a fuel will increase to 6,000,000 tons and as a gasoline additive 2,400,000 tons per year. Within 20 years one vehicle out of four will operate on methanol and only half of all vehicles on the planet will use gasoline. The efficiencies of aggregates for ammonia and methanol synthesis can be increased through improved methods of thermodynamic analysis making it possible to find the threshold limits for synthesis processes and their improvement, and determine the sources of losses and their elimination. The method for thermodynamic analysis consists of the following. First, equations are set up for quasilinear conversion of the starting material (methane) and for the end products (ammonia and methanol). These are then used to determine the energy requirements needed to produce a unit quantity of end product, the yield of secondary products, and the thermal effect of the process. These data are then used to find the theoretical energy required to produce the end product. Comparison of the theoretical energy with that of actual energy used to produce one ton of ammonia or methanol provides a basis for judging the efficiency of one or another process. References 31: 22 Russian, 9 Western.

UDC 541(64+127)

Spontaneous Polymerization Upon Interaction of N,N-Dimethylaminoethylmethacrylate With Allyl Chloride

18410044e Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 4 Jul-Aug 88 (manuscript received 25 Jan 88) pp 36-38

[Article by A. S. Maksumova, U. A. Safayev, A. T. Dahzlilov, and D. A. Topchiyev, Tashkent Order of Friendship of Peoples Polytechnical Institute imeni Abu Raykhana Beruni]

[Abstract] This article presents kinetic results from the reaction of the spontaneous polymerization of N,N-dimethylaminoethylmethacrylate (DMAEMA) with allyl chloride in absolute ethyl alcohol at 40°C. According to IR spectral data, spontaneous polymerization in this system involves only the quarternized monomer molecules, i.e., polymerization occurs upon the formation of the quarternary salt, with the allyl bond in the polymer being retained. The kinetic equation for the spontaneous polymerization of DMAEMA with allyl chloride in the presence of a monomeric quarternary salt is $V = 1.748 \cdot 10^{-5} [\text{DMAEMA}]^{1.04} [\text{allyl chloride}]^{0.92} [\text{DMAEMA allyl chloride}]^{1.82}$. References 7: Russian.

UDC 541.6

Modeling Solid-Phase Polymerization of Diacetylenes. I. General Principles

18410044g Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 4 Jul-Aug 88 (manuscript received 25 Jan 87) pp 50-55

[Article by G. A. Vinogradov, M. I. Gay, L. A. Gromov, M. M. Yelyashevich, and A. T. Mamdalimov, Institute of Chemistry and Physics of Polymers, UzSSR Academy of Sciences]

[Abstract] A study examined the solid-phase topochemical polymerization of diacetylenes (DA). This type of polymerization greatly limits the relative position of monomers in a DA monocrystal and their intermolecular interaction, yielding a single chemical reaction channel, which in turn leads to the formation of a stereoregular polymer chain with a near-perfect structure. The principles of a possible approach to modeling the polymerization reaction are studied, and several models are

suggested for describing the topochemical polymerization of DA. It is suggested that the principles of scaling be used to describe the polymerization. Figures 3, references 14: 2 Russian, 12 Western.

UDC 541 (14+64):543:943

Possibility of Stopping Photooxidative Degradation of Polyamides

18410075c Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 30 No 10, Oct 88 (manuscript received 28 Apr 87) pp 2064-2068

[Article by I. S. Lukomskaya, G. G. Makarov, L. M. Postnikov, and V. Ya. Shlyapintokh, Institute of Chemical Physics, USSR Academy of Sciences]

[Abstract] The role of 0.1 mol/kg azoisobutyric acid dinitrile (AAD) in the kinetics of the oxidative destruction of PA-548 industrial polyamide films was evaluated viscosometrically and manometrically. Thermal degradation was not observed either in an inert atmosphere or in oxygen at 75 to 98°. Liberation of nitrogen from AAD did not lead to any oxygen deficit in the polyamide film. AAD did not accelerate the benzoyl peroxide-induced destruction of the polyamide, but rather slightly inhibited it. The ratio of the gas pressure over the AAD-treated polyamide in an inert atmosphere to that in oxygen was constant over 10 hours of observation. This indicates that AAD and its products completely inhibit polyamide photooxidation. The rate constant of AAD photodecomposition was found to be 0.54 hr^{-1} . Tetracyanoethylene was found to partially inhibit polyamide photooxidation. The mechanism of the AAD action may also be via free radical acceptors, as is known for tetracyanoethylene. Figures 4; references 11: 6 Russian, 1 Hungarian, 1 Czech, 3 Western.

UDC 541(64+151):547.458.81)

Mechanism of Radiation-Induced Degradation of Cellulose and Its Derivatives

18410075d Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 30 No 10, Oct 88 (manuscript received 28 Apr 87) pp 2069-2075

[Article by Ye. P. Petryayev, V. V. Boltromeyuk, N. I. Kovalenko, and O. I. Shadyro, Scientific Research Institute of Physicochemical Problems, Belorussian State University imeni V. I. Lenin]

[Abstract] Radiation-induced degradation and functional group accumulation were studied in cellulose and its substituted derivatives. Trimethylcellulose and cellulose alkaline copper complex were found to undergo much less radiation destruction than does monomethylcellulose or cellulose. The effect was independent of atmosphere or degree of polymerization. The carbon dioxide yield in vacuum-irradiated samples was 0.2 molecules/100 eV for the trimethyl and copper derivatives. Over the radiation dose interval used, 10-150 kGy,

the concentration of functional groups increased in proportion to the dose absorbed. For cellulose and monomethylcellulose, carboxyl group formation predominated. For the trimethyl and copper complex derivatives, total functional group formation was much less. The data suggest that the formation of R_1 -type radicals predominates during radiolysis of cellulose and monomethylcellulose. The lactones formed are hydrolyzed to carboxylic acids during analysis. Esterification or complexation of the pyranose hydroxyls inhibits radiolysis due to steric factors and the inhibition of R_6 and oxygen radical formation. The main cause of carbonyl formation is R_4 -type fragmentation of the macroradical. The trimethylcellulose methyl group cleavage also occurs. References 17: 14 Russian, 3 Western.

UDC 541:539.3

Relationship Between Craze Formation and Shear Strain During Stretching of Cross-linked High-Density Polyethylene in Liquid Medium

18410075e Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 30 No 10, Oct 88 (manuscript received 22 May 87) pp 2165-2169

[Article by A. V. Yefimov, N. N. Valiotti, F. F. Sukhov, V. I. Dakin and N. F. Bakeyev, Moscow State University imeni M. V. Lomonosov]

[Abstract] The effect of radiation-induced cross-linking on the deformation of high-density polyethylene (HDPE) in a liquid medium was studied. The irradiated samples exhibited increased limits of forced elasticity in both air and methylethyl ketone (MEK). The effectiveness of MEK in lowering the elasticity limit decreased as the radiation dose increased. This effect was more pronounced at high deformation rates. Plotting the relative volume change versus relative deformation showed that 1.0 MGy decreased the contribution of craze formation to deformation whereas lower doses did not. Small-angle x-ray analysis confirmed decreased craze formation at higher radiation doses. At 0.75 and 1.0 MGy, shrinkage after stretching in MEK was greatly reduced, which is also indicative of reduced craze formation. The data

demonstrate that at high cross-link densities the stress of craze formation when samples of HDPE are stretched in liquid exceeds the stress of translational deformation. Figures 5; references 12: 7 Russian, 5 Western.

UDC 541.64:536.7

Effect of Cross-linking Extent on Phase Separation in Natural Rubber-n-Octadecane System

18410075b Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 30 No 10, Oct 88 (manuscript received 28 Apr 87) pp 2057-2063

[Article by A. L. Volnskiy, T. Ye. Grokhovskaya, G. M. Lukovkin, A. Sanches, and N. F. Bakeyev, Moscow State University imeni M. V. Lomonosov]

[Abstract] A study examined the relationship between the extent of cross-linking in natural rubber vulcanizates and their swelling in n-octadecane. The phase separation process was also investigated. The rubbers studied contained 1-8 weight percent dicumyl peroxide (DCP) plasticizer. Samples were soaked in n-octadecane for 3 hours and then cooled below the n-octadecane crystallization temperature. Increasing the DCP concentration resulted in a decreased degree of swelling, with the effect being more pronounced at lower concentrations. These systems are unstable over time, leading to separation of octadecane particles on the surface of the samples. Phase separation times ranged from 10 hours to over 1 year, with all samples approaching the levels of octadecane between 10 percent and 20 percent. The loss of octadecane was accompanied by a lowering of the melting temperature and observation of two transitions. The kinetics of octadecane exudation differ with the degree of rubber cross-linking due to the sol-phase and gel-phase nonhomogeneity of the rubber. Observations indicate that only that octadecane phase whose melting point is above room temperature migrates out of the rubber interior. More highly cross-linked rubbers are more heterogeneous and usually do not undergo complete homogenization on melting and resolidification. Decreases observed in the enthalpy of melting suggest that over time the octadecane becomes more dispersed in the rubber, which relieves residual stress in the lattice. Figures 6; references 3: 2 Russian, 1 Western.

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